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THE PREPARATION AND PROPERTIES OF COLLOIDAL MIXTURES.[1]

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It was by the well-known investigations of the English physicist Graham, published in the seventh decade of the last century, that the general attention of scientists was first drawn to the existence of a class of homogeneous mixtures, differing materially in their properties from ordinary solutions, such as those of salt and sugar. Impressed by the fact that the dissolved substance as a rule separates from the one class of solutions in the amorphous and often gelatinous state, and from the other in the form of crystals, he designated the former substances colloids and the latter crystalloids, and their solutions have since been commonly known respectively as colloidal and as crystalloidal or ordinary solutions. During the period immediately following Graham's classical researches, the subject of colloidal solutions received comparatively little attention. Within the last fifteen years, however, this field has become a favorite hunting ground of both physical chemists and physiologists in their searches after new truths, and greatly has the store of our knowledge in regard to this important state of aggregation been thereby increased. Yet the difficulty in reaching

[1] Presidential address delivered at the Philadelphia meeting of the American Chemical Society, December 29, 1904.

general conclusions as to the properties of these solutions has proved to be a very great one, owing to the complexity of the phenomena and to the apparent contradictions between many of the results obtained with different colloids and by different investigators. Moreover, the original literature of the subject has become so extensive and so detailed as to be almost overwhelming to one who, with limited time to devote to it, desires to obtain a general survey of this field of work. Therefore, although recently, several German monographs[1] upon the subject have appeared, it has seemed to me that a brief review of some of the more important principles thus far established might be of general interest to the members of this Society. I have had, however, not a little hesitation in undertaking to present to you even such an elementary account of the results attained as is here contemplated, for I have not myself been an investigator in this field and cannot claim even an intimate acquaintance with the original literature. I was led to make the attempt by the cordial assurances of assistance, which have been most amply fulfilled, from my colleague, Dr. J. C. Blake, who has been engaged in researches upon colloids for a number of years. I am greatly indebted also to Mr. Charles Field, 3rd, for his able and freely proffered assistance in the preparation of the experiments which I am to have the privilege of presenting to you as illustrations.

THE TWO CLASSES OF COLLOIDAL MIXTURES.

It seems appropriate to begin the consideration of the subject with a definition of the class of substances to which our attention is to be devoted. In accordance with the general use of the term, colloidal mixtures are most simply defined as liquid (or solid) mixtures of two (or more) substances which are not separated

[1] A. Lottermoser: "Anorganische Colloide," 1901, Ahrens Sammlung chemischer und chemisch-technischer Vorträge, 80 pages.—A Müller: "Die Theorie der Kolloide: Übersicht über die Forschungen, betreffend die Natur des Kolloidalzustandes," 1903, 56 pages. Fr. Deuticke, Leipzig und Wien.—G. Bredig: "Anorganische Fermente: Darstellung kolloidaler Mettalle auf electrische Wege und Untersuchung ihrer katalytischen Eigenschaften," 1901, 99 pages, W. Engelmann, Leipzig.—H. J. Hamburger: "Osmotischer Druck und Ionenlehre in der medicinischen Wissenschaften," 1904, Vol. III, pp. 58–106. J. F. Bergmann, Wiesbaden.—W. Pauli: "Der kolloidale Zustand und die Vorgänge in der lebendigen Substanz," 1902, Vieweg und Sohn, Braunschweig.

from one another by the action of gravity however long continued nor by filtration through paper, but which are so separated when the liquid is forced through animal membranes, the substance then remaining behind being designated the colloid. This distinguishes them on the one hand from suspensions of fine visible particles, and on the other from ordinary solutions, and it implies that the colloidal particles are intermediate in size between the particles of such suspensions and the molecules which are present in ordinary solutions. It is obvious, however, that this definition is not based upon a really fundamental dstinction either in the properties exhibited by the various mixtures or in the character of their particles. It would, therefore, not be surprising to discover that the so-defined group of colloids include substances having very different properties in other respects than that just considered. The first result of the researches upon colloids which I wish especially to emphasize is that there are in fact at least two kinds of dissolved or suspended substances retained by animal membranes, which differ so radically in their other properties that their inclusion in the same class is sure to lead to serious confuslon, unless special pains be taken to discriminate between them. I shall therefore distinguish two sub-classes of colloidal mixtures. As types of these I would draw your attention to these aqueous solutions of gelatine and of colloidal arsenious sulphide. The former class possesses a much greater viscosity than that of water; the latter does not appreciably differ from it in this respect (Expt.).[1] The former gelatinizes upon cooling or upon evaporation, and passes again into solution upon heating or addition of the solvent; the latter does not gelatinize upon cooling, and if gelatinized by other means it does not redissolve upon heating (Expt).[2] The former is not coagulated by the addition of salts (unless in excessive amount),[3] the latter immediately

[1] A large test-tube containing a 1 per cent. solution of gelatine in water and one containing a colloidal suspension of arsenious sulphide were shown, each being shaken to indicate the viscosity.

[2] Two tubes with the same contents as before, but previously brought to 0° by immersion in ice water, were shown.

[3] A very large quantity of any salt may, by reason of its osmotic or dehydrating action, cause a precipitation of the colloid, but this effect is quite distinct from the coagulation of colloidal suspensions, which is produced by a relatively small quantity of a salt and by a quantity varying greatly with the valence of its ions.

gives an abundant precipitate (Expt.).[1] We have therefore to distinguish the viscous, gelatinizing, colloidal mixtures, not coagulated by salts, from the non-viscous, non-gelatinizing, but readily coagulable mixtures. The former class I shall designate *colloidal solutions*, the latter, *colloidal suspensions*. This nomenclature[2] is adopted in the belief, held also by others,[3] that a more fundamental distinction between the two classes of mixtures is the possession by the former of the characteristic properties of true solutions—osmotic pressure, diffusibility, and usually a limited solubility of the colloid at some temperature, and the absence of these properties in those in the latter class, and the manifestation by them of many similarities to macroscopic and microscopic suspensions. Even though this may not be a sharp line of division, it is highly probable that typical members of two classes exhibit these properties of true solutions in such a different degree as to make the differentiation an important one. Unfortunately, however, colloidal mixtures have not yet been satisfactorily enough investigated with respect to these properties to enable a classification to be based exclusively upon them.

COLLOIDAL SOLUTIONS.

I will now proceed to discuss the characteristics of the two classes as manifested by typical representatives, first briefly considering the colloidal solutions. These substances are, for the most part, obtained directly from animal or vegetable sources and are purified by dialysis. Among the most important are gelatine, agar-agar, unheated albumen, caramel, starch, dextrine, and many natural gums.

A number of the important properties of these colloidal solu-

[1] To a tube half-filled with a 1 per cent. gelatine solution and to one half-filled with a colloidal suspension of arsenious sulphide 10 cc. normal magnesium chloride solution were added. No effect was observed in the first tube; a voluminous yellow precipitate resulted in the second.

[2] As Dr. Blake suggests to me, it might be better to confine the term colloid to the mixtures of the first class, since Graham applied it only to these and since it literally signifies glue-like or gelatinous, and to designate mixtures of the second class by a new term which will not suggest any relationship to those of the first class. The universal application of the term colloid to both classes and the difficulty of finding a new descriptive term for the latter class seem to make the compromise here proposed more practicable.

[3] Müller: *Ztschr. anorg. Chem.*, **36**, 344 (1903); Bechhold: *Ztschr. phys. Chem.*, **48**, 393 (1904).

tions have already been alluded to, but some of them deserve further consideration. The contrasts and similarities between them and ordinary solutions may first be mentioned. Such colloids possess a much slower rate of diffusion, a much smaller osmotic pressure, and a much slighter influence on the vapor-pressure, freezing-point, and boiling-point of the solvent than do corresponding weights of crystalline substances. So small are these effects that whether they exist at all is a question to which much investigation and discussion has been devoted. The now existing experimental data seem to show, however, that the gelatinizing non-coagulable colloids do possess these properties and influences in an appreciable degree. The results of the osmotic pressure determinations in the cases where it has been measured against a parchment or animal membrane, which would not retain the mineral impurities, are especially significant. Thus by this method it was found by Pfeffer[1] that a 6 per cent. glue solution and by Linebarger[2] that a 2.5 per cent. tungstic acid solution exerted a pressure of about one-third of an atmosphere, and by Starling[3] that a 10 per cent. solution of the colloids of blood-serum produced one of 40 mm. of mercury. Further investigations in this direction would be of great value. The results of Graham,[4] too, seem to leave no doubt as to the existence of diffusion; he found, for example, that albumen diffused one-seventh as fast, and caramel one-fourteenth as fast as cane-sugar. Thus, these colloids exhibit the same properties as ordinary dissolved substances, but in a lesser degree—a fact which is explained in accordance with the modern theory of solutions by the simple assumption that they are true solutions, but that their molecules consist of aggregates of the ultimate chemical molecules and are therefore of much greater weight and complexity than those of non-colloidal substances.

This assumption seems, however, of itself alone, scarcely sufficient to account for the abnormal viscosity of these colloids, their power of gelatinization, and their property of permitting the free passage through them of non-colloidal substances but preventing entirely that of other colloids of either of the two classes. This last property is the same one that is involved in the permeability

[1] "Osmotische Untersuchungen," 1877.
[2] *Am. J. Sci.*, **143**, 218 (1902).
[3] *J. Physiol.*, **24**, 320 (1899).
[4] *Phil. Trans.*, **151**, 185 (1861).

of animal membranes for crystalloids and their impermeability for colloids, since such membranes are themselves nothing more than gelatinized colloids. Yet it deserves, on account of its great importance, a somewhat fuller consideration. This difference in behavior towards crystalloids and colloids may be readily illustrated by immersing sticks of gelatine or agar jelly in one experiment in a colored salt solution and in another in a colored colloidal suspension, and allowing them to remain for a day or more. Such experiments are in progress in these vessels, one of which contains a solution of copper sulphate and ammônia and the other a colloidal suspension of ferric ferrocyanide or Prussian blue. Sticks of agar jelly were placed in each of these two days ago. Upon removing the sticks and cutting them in two (Expt.),[1] it will be noticed that the ammoniated copper sulphate has permeated the stick uniformly to its center while the Prussian blue has not entered it at all.

Not only are gelatinized colloids permeable to salts, but, remarkably enough, they offer only a very slight, often scarcely appreciable, hindrance to the passage of these substances through them. Thus, the accurate experiments of Voigtländer[2] have shown that the rate of diffusion of salts and mineral acids is the same, at any rate within 1 per cent., in a solid jelly containing 3 to 5 per cent. of agar-agar as it is in one containing only 1 per cent. of agar-agar, and it is therefore presumably the same as in water itself, though the accuracy with which this latter conclusion has yet been directly tested is much less. It has also been shown by the measurements of Arrhenius that the electrical conductivity of salts in a gelatine jelly is only a few per cent. different from that in pure water, and that there is no sudden change in its value when the jelly sets. This property is, however, dependent on the rate of motion of the ionized molecules of the salt through the medium between the electrodes, and the slight variation in

[1] Two cylindrical sticks, 5 cm. in diameter and 15 cm. in height, of a 4 per cent. agar jelly had been prepared by pouring the hot liquid solution into large glass tubes corked at one end, allowing the mass to cool, and pushing out the solid sticks. One of these had been placed in a nearly saturated copper sulphate solution to which enough ammonium hydroxide was added to redissolve the precipitate first formed. The other had been placed in a colloidal suspension of Prussian blue made by mixing equal volumes of 0.02 molal solutions of ferric chloride and potassium ferrocyanide.

[2] *Ztschr. phys. Chem.*, **3**, 329–331 (1889).

it caused by the presence of colloids, even in quantity sufficient to produce gelatinization, proves that the flow of such molecules is but little impeded by the colloid.

Returning now for a moment to the other side of the phenomenon—the impermeability of one colloid by another, attention may be called to an apparently related fact of much importance, namely, to the fact that the presence of a gelatinizing colloid in a liquid in fairly small quantity prevents the coagulation of colloidal suspensions by salts, and therefore usually prevents the formation of a coagulated precipitate when the solutions of two chemical substances are mixed which, under ordinary conditions, give rise to such a precipitate. Thus when aqueous solutions of silver nitrate and sodium chloride are mixed, an abundant curdy precipitate is produced, but, if a little gelatine solution be first added to one of the salt solutions, only an opalescence results, and the silver chloride formed by the metathesis remains indefinitely in the state of a colloidal suspension (Expt.).[1] Glycerol, sugar, and even ether in some cases have a similar influence. This result may arise from the fact that in the presence of the gelatine the particles of silver chloride after attaining a certain size are not capable of diffusing, and hence of coming into contact with one another. Bechhold,[2] however, has made it probable that, at any rate in many cases, the gelatine prevents the coagulation in another way, namely, by forming an envelope around the solid particle. Whatever may be the explanation of the phenomenon, it is one of great technical importance, especially in relation to photography, for upon it is based the preparation of the so-called emulsions of silver salts in gelatine, collodion, or albumen with which dry plates, films, and printing-out paper are coated.

Recent investigations, especially those of Bütschli,[3] van Bem-

[1] 200 cc. of a 0.05 molal silver nitrate solution containing 2.5 per cent. nitric acid (sp. gr. 1.42) were mixed in a lecture jar with 200 cc. of a 0.05 molal sodium chloride solution; a curdy white precipitate separated immediately. The experiment was then repeated with solutions of the two salts of the same concentration as before in each of which 1 per cent. of gelatine had been dissolved; the mixture became opalescent at once, and the milkiness had greatly increased in fifteen minutes, but no coagulation of the precipitate occurred even on long standing.

[2] *Ztschr. phys. Chem.*, **48**, 396 (1904).

[3] "Untersuchungen über microscopische Schäume und das Protoplasma," Leipzig, 1892; "Ueber den Bau quellbarer Körper und die Bedeutung der Quellung, Göttingen," 1896; "Untersuchung über Structuren," Leipzig, 1898. These references are cited from Müller's "Theorie der Colloide."

melen,[1] and Hardy[2] have proved that the gelatinization of these colloidal solutions arises from the separation of a portion of the colloid in the solid state in more or less continuous masses. The resulting jelly, or gel, as it is technically called, has been shown to have an irregular sponge-like structure, the web consisting of a solid solution of the two substances and the interstices being filled with a liquid solution of them. This has been proved in some cases by direct microscopic observation, and in others, by separating the liquid from the solid portion by pressure and by analyzing these portions, which were thus shown to have a very different composition with respect to the proportions of the two constituents. Thus Hardy[1] states that when a solution of 13.5 grams of gelatine in a mixture of 50 cc. of alcohol and 50 cc. of water is gradually cooled, it remains homogeneous until a temperature of 17° is reached. Then it separates into two liquid phases, and is seen to consist of small microscopic droplets suspended in a fluid matrix. As the temperature falls, these droplets cohere to one another and at 12° they have become solid, forming a framework built up of little spherical masses. The mixture as a whole has then become a jelly. At 14° the droplets were separated and found to contain 18 per cent. of gelatine while the matrix contained only 5.5 per cent. The important statement is also made that the first appearance of the droplets is attended by a great increase in viscosity, while the subsequent increase is a continuous one. The abnormal viscosity of such colloidal mixtures is therefore probably always due to a physical heterogeneity of this kind. The investigations made with other gelatinizing colloids, such as agar, albumen, starch, and even silicic acid, have led to a similar conclusion in regard to the structure of the jelly.

COLLOIDAL SUSPENSIONS.

Methods of Preparation.—The mixtures of this class have been, for the most part, prepared artificially. I will therefore first describe the principles of some of the methods which have been employed for this purpose.

Of these principles the most important one is, that when an insoluble substance is produced *in the absence of electrolytes* by a reaction between two chemical compounds, it almost invariably

[1] *Ztschr. anorg. Chem.*, **18**, 14 (1898).

[2] *J. Physiol.*, **24**, 176 (1899).

separates in the state of a colloidal suspension. Electrolytes must not be present in considerable quantity for the reason that ions coagulate these suspensions. Thus, when I add a solution of hydrogen sulphide, a slightly ionized substance, to one of arsenious oxide, also slightly ionized, no coagulated precipitate of arsenious sulphide results, but only a turbid yellow liquid, which, when poured through filter-paper, leaves nothing behind (Expt.).[1] It will be noted that in this case the other product of the reaction is water, an un-ionized compound. If this reaction had been carried out with a solution of arsenious chloride, instead of with that of the oxide, the ordinary precipitate of arsenious sulphide would, of course, have been obtained, for, in this case, the hydrochloric acid produced by the reaction, being largely dissociated into hydrogen and chlorine ions, coagulates the colloidal suspension. Thus, upon adding some hydrochloric acid to this mixture, a large precipitate is immediately produced (Expt.).[2] As a second illustration of this method, I will add hydrogen sulphide water to a solution of mercuric cyanide (Expt.).[3] In this case also a colloidal suspension of the sulphide results, for the three substances involved in the reaction, hydrogen sulphide, mercuric cyanide, and hydrocyanic acid, are non-electrolytes; but, upon the addition of hydrochloric acid, or still better of magnesium chloride, to this solution, the precipitate immediately coagulates (Expt.).[4] It is not necessary, of course, that electrolytes be entirely excluded, but only that they be not present at any point at such a concentration as will produce coagulation. The method is, therefore, of fairly general applicability. Thus a colloidal suspension of Prussian blue can be prepared by mixing dilute solutions of nearly equivalent quantities of ferric chloride and potassium ferrocyanide, for the product of

[1] To 200 cc. of a 1 per cent. solution of arsenious oxide (prepared by boiling 12 grams of the solid with water for fifteen minutes, cooling, and filtering), 200 cc. of saturated hydrogen sulphide water were added. The mixture was then poured through a ribbed filter.

[2] To the arsenious sulphide suspension just prepared, 10 cc. HCl (sp. gr. 1.12) were added.

[3] 200 cc. $\frac{1}{8}$ molal $Hg(CN)_2$ solution and an equal volume of saturated hydrogen sulphide water were poured simultaneously into a lecture jar; a black liquid resulted. The resulting colloidal mixture was poured through a ribbed filter; scarcely any precipitate remained on the filter.

[4] To the suspension just prepared, 10 cc. normal $MgCl_2$ solution was added.

the reaction, potassium chloride, has a coagulating effect only at higher concentrations (Expt.).[1]

A second method which has, at any rate until recently, been even more commonly employed than that just described, consists in the dialysis of a salt solution in which a colloidal base or acid is present, either owing to natural hydrolysis or to the previous addition of an alkali or acid. Thus colloidal silicic acid may be prepared by dialyzing either a solution of sodium silicate alone, or one to which hydrochloric acid has been previously added. Colloidal ferric hydroxide is obtained by the dialysis of a ferric chloride solution which has been treated with ammonium carbonate until a permanent precipitate begins to form. Here is a suspension of this substance which has been prepared in this way (Expt.).[2] This process of dialysis is commonly resorted to also for freeing colloidal solutions or suspensions prepared in other ways, from mineral impurities. It is most conveniently carried out in parchment tubes, which are now an article of commerce. As the surface exposed by these is large, the process is a comparatively rapid one. The solution to be dialyzed is placed within such tubes, and these are immersed first in running tap water and afterwards in distilled water which is frequently renewed (Expt.).[3]

There is one other method of sufficient importance to deserve mention, and this is the process described by Bredig of preparing colloidal suspensions of metals by producing an electric arc under water between electrodes of the metal in question. This is most readily carried out with the non-oxidizable metals, such

[1] 200 cc. of a 0.02 molal ferric chloride solution and 200 cc. of a 0.02 molal of potassium ferrocyanide solution were simultaneously poured into a lecture jar: a dark blue liquid resulted. Of this mixture, 50 cc. were added to 300 cc. water: the liquid was then seen to be perfectly clear.

[2] A dark red but perfectly clear colloidal suspension of ferric hydroxide was exhibited. This had been prepared by adding to a molal ferric chloride solution a molal ammonium carbonate solution until the precipitate forming on each addition would barely dissolve. The mixture was next dialyzed, first against running tap water, then against distilled water, and finally against conductivity water. It was then filtered and diluted with an equal volume of conductivity water. The solution, which now contained 2.40 grams Fe_2O_3 per liter, had a specific conductance of only 35×10^{-6}. This solution was used in all the subsequent experiments with this colloid.

[3] Such a dialyzing arrangement as is here described was exhibited.

as gold or platinum, in the manner here illustrated (Expt.).[1] The method depends on the fact that the metal is volatilized into the arc or spattered into it in an extremely finely divided form, and is then condensed or absorbed by the water, which, owing to the absence of electrolytes, has little tendency to cause aggregation of the particles.

Besides these colloidal suspensions artificially prepared from mineral substances, others can be obtained by dialysis and other treatments from animal and vegetable sources. Among the most fully investigated of these are heated albumen and gum mastic.

Properties Indicating Heterogeneity.—Turning now to the properties of such colloidal suspensions, it seems appropriate first to refer to those which indicate that these mixtures really are suspensions of minute particles and not true solutions, or, in the language of modern physical chemistry, that they are heterogeneous, two-phase systems. The fact that the components of the mixture are separated by filtration through animal membranes or close-grained porcelain filters is not of itself an evidence of physical heterogeneity, for by copper ferrocyanide membranes, such as Pfeffer first prepared, which differ from these presumably only in the size of their pores, sugar and even salts can be separated from true solutions. In some cases, the presence of particles in suspension in so-called colloidal mixtures has been proved directly by microscopic observation;[2] thus this is the case with the colloidal mercuric sulphide and with colloidal arsenious sulphide when prepared under certain conditions, but not under others; the same is true of blue colloidal gold, which can be produced in a variety of ways, for example, by the reduction of gold chloride solution by hydrazine. In most cases, however, the colloidal

[1] Each of two gold wires 1.5 mm. in diameter and 8 cm. long was inserted in a binding post screwed into a wooden handle. The wires both dipped about 2 cm. below the surface of a 1/2000 normal hydrochloric acid solution contained in a 12 cm. crystallizing dish. One wire was held firmly in position by a clamp upon its handle; the other was held loosely by a clamp, but was also grasped by the hand, whereby its end could be kept at such a distance from the end of the other wire as to form and maintain an arc. The gold wires were connected through a coil of nickel steel wire of 12 ohms resistance with the terminals of a 110-volt direct-current circuit. Red clouds of colloidal gold were formed near the arc, and in half a minute the whole liquid had assumed a red color.

[2] It would seem best to designate such mixtures microscopic suspensions, and to confine the term colloidal suspensions to those whose particles have a size beyond the limit of microscopic visibility, it being, of course, understood that there is no fundamental distinction between them.

particles can not be seen even under the best conditions; they are, therefore, smaller than one-seventh of a micron (1/7000 mm.), which is about the limit of microscopic visibility. It will be of great interest to determine whether they can not be detected in many other cases with the help of the new Zeiss microscope, which, by employing quartz lenses and ultraviolet light (having a much shorter wave-length than ordinary light) and obtaining the image photographically, extends the limit of visible diameters to about one-half of its present value. With such an "ultramicroscope" Raehlmann[1] has already observed the suspended particles in an albumen solution. By the optical method of Siedentopf and Zsigmondy,[2] in which the colloidal mixture is intensely illuminated by a thin beam of light, and the diffused light reflected from the suspended particles at right angles to the beam is viewed with a powerful microscope, the presence of still smaller particles having a diameter of 1/100 micron, has been detected in red-gold suspensions and in other colloidal mixtures.

A strong indication of the heterogeneity of colloidal suspensions is furnished also by the familiar optical phenomenon which is often called the Tyndall effect; namely, when a beam of light is passed through any medium containing particles in suspension, the beam becomes visible, as does a sunbeam in dusty air, owing to a diffuse reflection of light from the particles. This can readily be shown to occur with colloidal suspensions of gold and of arsenious sulphide, such as were prepared a few minutes ago (Expt.).[3] Moreover, in every case where reflection takes place from non-metallic surfaces the reflected light is polarized, and this is found, in fact, to be true of the rays diffusely reflected from a colloidal suspension by examining them with a Nicol prism (Expt.).[4] It has been shown by Lobry de Bruyn,[5] to be sure, that not only colloidal solutions (colloidal mixtures of the first class), but also

[1] *Berl. klinische Wochenschrift*, 1904, p. 186.

[2] *Ztschr. Elektrochem.*, **8**, 864 (1902).

[3] A beam of light from a projection-lantern, made smaller by covering the lens with a diaphragm with a circular aperture 1 cm. in diameter, was thrown into a colloidal gold suspension in a rectangular jar placed 15 cm. in front of the lens; the path of the beam in the liquid was strongly luminous.

[4] A Nicol prism was inserted between the lantern and the colloidal suspension, and the Nicol was slowly rotated; the light in the liquid was seen to be much brighter in some positions of the Nicol than in those at right angles to them.

[5] See Hamburger's "Osmotischer Druck und Ionenlehre," Vol. 3, p. 63.

ordinary solutions of some substances with complex molecules like sugar exhibit this phenomenon, so that it is not a decisive criterion of a suspension. They do so, however, in an incomparably less degree than do typical colloidal suspensions, so that it at least furnishes evidence that the particles in the latter mixtures are of much larger size than are those in the former.

Whether the well-defined colloidal suspensions possess in appreciable degree what may well be regarded as the best single criterion of a true solution—a measurable osmotic pressure—does not, in spite of its importance, seem to have been the subject of investigation by the direct osmotic method. Nor is there conclusive evidence that they show the closely related phenomenon of diffusion.[1] If the existence of these properties to an extent corresponding at all to the size and number of the particles should be demonstrated, it would, of course, prove that the distinction between colloidal solutions and suspensions is not one of quality, but only one of degree.

Properties Related to the Electrification of the Particles.—I will next consider a quite distinct class of properties, which depend not on the size of the colloidal particles, but apparently upon the presence of electric charges upon them.

The most direct evidence of this electrification is furnished by the migration of the colloidal particles through the liquid under the influence of an applied electromotive force—a phenomenon that was first extensively studied by Picton and Linder[2] in 1897, but which has since been further investigated by several other workers.[3] This effect I will illustrate with the colloidal suspensions of arsenious sulphide and ferric hydroxide with which these two U-tubes are filled. The upper ends of the U-tubes are covered with goldbeaters' skin and are surrounded by wider tubes containing pure water in which platinum electrodes are

[1] It is true that Whitney and Blake (this Journal, **26**, 1361 (1904)) have shown that red colloidal gold which had been migrated under a potential-gradient to the foot of a vertical tube covered with goldbeaters' skin immediately began to diffuse upward when the electric field was destroyed and did so at a rate comparable with that of salts, but it seems possible that the phenomenon was due to some counter-electrical effect.

[2] *J. Chem. Soc.*, **71**, 568 (1897).

[3] For a review of the preceding investigations upon the migration of colloids and for a description of the most accurate work thus far executed see the recent article of W. R. Whitney and J. C. Blake: This Journal, **26**, 1339–1387 (1904).

placed, so that the products of electrolysis collecting around them may not influence the colloid. I will connect these tubes in parallel with the terminals of a 110-volt circuit in such a way that the current will flow through each of them in the direction from left to right, as will be shown by the copper coulometer in series with them. (Expt.)[1] It will be some minutes before any result will be observed. Then it will be seen that the ferric hydroxide has moved down with a sharp surface of demarkation on the side where the current enters, leaving a clear layer of water above, and that the arsenious sulphide has done the same but on the opposite side of the tube. In other words, the ferric hydroxide particles are migrating with the positive current towards the cathode, the arsenious sulphide with the negative current towards the anode. The former are therefore positively, and the latter negatively charged. These results are typical ones—the same behavior is exhibited by all colloidal suspensions, and, it may be added, also by fine microscopic suspensions, such as those of quartz, kaolin, and lampblack. Other basic hydroxides, like those of aluminum, chromium, and thorium, and certain dyestuffs migrate to the cathode just as does that of iron. The suspended particles of almost all other substances, whether colloidal or microscopic, migrate to the anode. This is true, for example, of silicic acid, stannic acid, metallic sulphides, salts like silver

[1] The U-tubes employed were 15 cm. in total height and had a bore of 3 cm. Over the tops of the tubes goldbeaters' skin was tied. At the bottom of the bend was a hole 1 cm. in diameter. The tubes had been completely filled before the lecture by inverting them and pouring the colloidal mixtures in through this hole, which was then closed by slipping a rubber band over it. Over each arm of each tube a straight tube of only slightly greater diameter was placed. These extended downwards nearly to the top of the bend of the U-tube and were there united to the latter by a rubber band. They also extended 5 cm. above the goldbeaters' skin at the top of the U-tubes. These outside tubes were filled with conductivity water. The colloidal suspensions had been prepared as described above, and had been dialyzed for a week, first against distilled water and finally against conductivity water. This must be done in order to remove electrolytes as completely as possible, since otherwise the heat produced by the current causes convection and disturbance of the migrating surface. The electrical connections were made with large wires, so as to be readily seen, in the way stated above. A 220-volt circuit, if available, is to be preferred. The copper coulometer referred to consisted of a thick copper wire as anode, and a strip of platinum foil as cathode, placed in a beaker containing a very dilute copper sulphate solution.

iodide and Prussian blue, and metals like gold and platinum. Of special interest with reference to the explanation of the phenomenon is the fact discovered by Hardy[1] that an egg-albumen suspension migrates towards the cathode in an acid liquid and towards the anode in an alkaline one.

In regard to the cause and character of the electrification two assumptions deserve consideration: one is that it is simply an example of contact electricity, the colloid particle assuming a charge of one sign and the surrounding water one of the other. This correlates this phenomenon of migration with that of electrical endosmose; for the motion of suspended kaolin, for example, through water against the positive current is obviously the converse of the flow of water through a porous clay diaphragm with the current. It does not, however, give an obvious explanation of the facts that the basic colloidal particles become positively charged and the acidic and neutral ones negatively charged, or of the peculiar behavior of albumen. The other assumption accounts for these facts. According to it the phenomenon is a simple case of ionization, the character of which may be best illustrated by specific examples. Thus, each aggregate of ferric hydroxide molecules may dissociate into one or more ordinary hydroxyl ions and a residual positively charged colloidal particle, and each aggregate of silicic or stannic acid molecules into one or more hydrogen ions and a residual negatively charged colloidal particle. Albumen, which is known to be capable of forming salts with both acids and bases, would, acting as a salt, dissociate into an ordinary positive ion and a colloidal negative one in alkaline solution, and into an ordinary negative ion and a colloidal positive one in acid solution. To explain the behavior of neutral substances like gold or quartz by this hypothesis, it is necessary to supplement it by the assumption that in these cases it is the water or other electrolyte combined with or adsorbed by the colloidal particles which undergoes ionization. It seems not improbable that there may be truth in each of these hypotheses, contact electrification occurring in the case of the coarser suspensions, and ionization in the case of those which approximate more nearly to colloidal solutions. It should be noticed that these hypotheses do not differ as to the charge on the colloidal particle itself, the existence of which is in fact experimentally demon-

[1] *J. Physiol.*, **24**, 292 (1899); *Ztschr. phys. Chem.*, **33**, 387 (1900).

strated, but only as to the location of the accompanying charge of opposite sign, namely, as to whether it is on the water itself or on ordinary ions dissolved in it. This matter is not essential to our further considerations.

The migration of colloids under a potential-gradient is not only of great theoretical importance in showing that the particles are electrified, but it is also of much experimental value from the standpoint of the exact investigation of these substances, since, as Whitney and Blake[1] have shown, it furnishes the most perfect method we have of obtaining colloidal suspensions free not merely from dissolved but from adsorbed electrolytes. This method may therefore be briefly described, using red colloidal gold as an example. If a suspension of this colloid, purified as far as possible by dialysis, be migrated downwards in a vertical tube whose ends are covered with goldbeaters' skin and are surrounded by larger tubes containing pure running water in which the electrodes are placed, the gold finally collects as a thick mud on the goldbeaters' skin at the bottom, while the electrolytes pass out in large part into the liquid around the electrodes (Expt.).[2] If now the liquid in the tube be drawn off and the mud be added to pure water, it immediately passes again into the state of colloidal suspension (Expt.),[3] and the migration can then be repeated if desired. In this way a gold suspension has been prepared which had an electrical conductivity only about twice as great as that of the double-distilled water ordinarily used in conductivity work. Moreover, it is evident that a colloidal solution of any concentration can be prepared by this method. Many other colloids also, such as colloidal silver or Prussian blue, which can be obtained in the solid state either by this method or by filtration, evaporation, or coagulation, immediately form again a colloidal suspension on the addition of pure water (Expt.).[4]

[1] This Journal, **26**, 1345 (1904).

[2] The apparatus, as here described, containing a red gold suspension which had been migrated down, leaving a colorless liquid above the gold mud collected on the goldbeaters' skin, was exhibited.

[3] The tube was quickly inverted, whereupon the gold mud disseminated itself through the colorless liquid beneath, yielding an apparently homogeneous red solution.

[4] A few centigrams of dry colloidal silver were added to 500 cc. of water; a turbid brown liquid resulted. The colloidal silver had been prepared by mixing a silver nitrate solution with a solution of tannic acid in ammonia, filtering the mixture with the help of suction through a porous cup, scraping off the mud from the wall, and drying it in the air.

Passing over, because of lack of time, some interesting facts in regard to the conductivity and rate of migration of pure colloids, I will turn now to the extremely important phenomenon of their coagulation. It will be seen that this phenomenon is certainly closely related to the electric charges on the colloidal particles. Indeed, it seems highly probable that they remain in suspension because of their electrification. Thus Hardy[1] found that egg-albumen, whose particles are shown by their migration to be positively charged in acid solution and negatively in alkaline solution, immediately coagulate when the solution is made neutral. I would also call your attention to another interesting fact having, apparently, the same significance, namely, to the fact that when two colloidal suspensions, whose particles have an electric charge of the same sign, are mixed, they have no influence upon each other, but when two suspensions, with particles oppositely electrified, are brought together, the two colloids combine with each other, and with proper proportions a complete coagulation results. Thus, upon mixing these suspensions of colloidal gold and of arsenious sulphide, no coagulation occurs (Expt.),[2] but when the suspensions of ferric hydroxide and arsenious sulphide, which we have seen from their behavior on migration have opposite electric charges, are poured together, there is immediate coagulation, and in a few minutes the precipitate settles, leaving the liquid clear above (Expt).[3]

Ordinary dissolved substances are also to be divided into two classes with respect to their effect in coagulating colloids. Non-electrolytes, whether organic or inorganic, have no tendency to produce coagulation; indeed, organic substances, like ether, glycerol, or sugar, often increase the stability of the suspension. On the other hand, strong electrolytes, that is, substances, which

[1] *J. Physiol.*, **24**, 292 (1899).

[2] 200 cc. of a colloidal gold suspension (previously made by adding an ethereal solution of dry auric chloride to an aqueous solution of acetylene and dialyzing) were mixed with 200 cc. of a colloidal arsenious sulphide suspension.

[3] 150 cc. of the dialyzed ferric hydroxide suspension, prepared as described in a preceding foot-note, and 200 cc. of the dialyzed arsenious sulphide suspension were poured simultaneously into a lecture jar; a large flocculent precipitate of a color intermediate between that of ferric hydroxide and arsenious sulphide formed at once and soon settled, leaving the liquid nearly clear above. The right proportions of the two colloids to give rise to complete precipitation must be determined by trial for any pair of preparations.

are themselves largely dissociated into electrically charged particles or ions, cause coagulation, when their concentration in the solution becomes sufficiently great. Although complete coagulation does not occur suddenly as the quantity of electrolyte is increased, yet the interval between the concentration at which, in a given time, the particles become visibly larger and that at which they have become large enough to settle out or to be retained by a filter is usually so small that a fairly definite concentration can be specified at which each electrolyte causes a certain, experimentally determinable, degree of coagulation in a definite time.[1] Now recent investigations have demonstrated the remarkable fact that this coagulation-concentration is nearly the same for different ions having the same electric charge (or valence), but that it diminishes enormously with increase of the electric charge of the ion of unlike sign to that of the colloid, while it is not affected by a change in the electric charge on the ion of like sign.

These principles are well illustrated by the results given in the table, which were obtained by Freundlich,[2] on the one hand with the negative colloid, arsenious sulphide, and on the other with the positive colloid, ferric hydroxide, by determining the concentration which in two hours caused such coagulation as would prevent any of the colloid from passing through a hardened filter.

Coagulation-concentration in milli-equivalents per liter.

of As_2S_3, a negative colloid, by			of FeO_3H_3, a positive colloid, by	
NaCl... 71	$MgCl_2$..... 2.0	$AlCl_3$..... 0.39	NaCl... 9.3	K_2SO_4... 0.41
KNO_3. 70	$Ba(NO_3)_2$. 1.9	$Al(NO_3)_3$.. 0.41	KNO_3.. 11.9	$K_2Cr_2O_7$. 0.39
K_2SO_4. 91	$MgSO_4$..... 2.3	$Ce_2(SO_4)_3$. 0.40	$BaCl_2$.... 9.6	$MgSO_4$.. 0.43

I can also roughly illustrate these principles by experiments with these two colloids.[3]

[1] That the phenomenon really consists in a different *rate* of coagulation at different concentrations, and not in an equilibrium established at any definite concentration, has been emphasized by Freundlich (*Ztschr. phys. Chem.*, **44**, 143 (1903)). Unfortunately, there has been no systematic investigation of the matter in this direction in spite of its great importance as a help in explaining the mechanism of the coagulation.

[2] *Ztschr. phys. Chem.*, **44**, 135, 151 (1903).

[3] Separate 50 cc. portions of an arsenious sulphide suspension (made by mixing equal volumes of a 1 per cent. As_2O_3 solution and of a saturated hydrogen sulphide solution and filtering) were poured into a row of conical lecture jars each of which contained already 200 cc. of a solution of one of

It is evident from these facts that it is the ion with a charge opposite to that of the colloid particles that is mainly responsible for their coagulation, but what the mechanism of this coagulation is, is not yet understood, though it has been the subject of much discussion. Interesting though they are, I shall not try to describe the explanations that have been suggested; for, in my opinion, mere speculative hypotheses, that is, hypotheses which have not been shown to facilitate to an important extent a knowledge of the actual phenomena, are of little value except to the investigators of them, and to them only because of the possibility of their future development into really useful conceptions. The recent literature of colloids furnishes a striking example of the unfortunate tendency even of our modern investigators and text-book writers to attach greater importance to hypothetical interpretations of imperfectly known phenomena than to a determination and presentation of the laws in regard to them.

Even an elementary consideration of the properties of colloids should include a discussion of the absorption or co-precipitation of other substances with them when they are gelatinized or coagulated—a phenomenon which is of great importance in analytical chemistry, as well as in other directions. But, as I fear this lecture has already exceeded its normal length, I shall have to omit entirely this side of the subject.

I shall, too, have to content myself with a mere reference to the importance of a knowledge of the properties of colloids not only in the industrial applications of chemistry, but also in many other sciences and arts. Mention can only be made of the facts that the industries of dyeing, of tanning, and of glass-making and

the following substances having the concentration in milli-equivalents per liter shown by the numbers preceding the symbols: (1) 0.6, $AlCl_3$*; (2) 1.5, $MgCl_2$; (3) 20, $MgCl_2$*; (4) 60, NaCl; (5) 400, NaCl*; (6) 60, Na_2SO_4; (7) 400, Na_2SO_4*. Separate 50 cc. portions of a ferric hydroxide suspension, prepared as described in a preceding foot-note, were also added to 200 cc. portions of the following solutions having the indicated concentrations in milli-equivalents per liter: (1) 0.02, $K_3Fe(CN)_6$; (2) 0.1, $K_3Fe(CN)_6$*; (3) 0.1, Na_2SO_4; (4) 1.6, Na_2SO_4*; (5) 5, NaCl; (6) 50, NaCl*; (7) 5, $MgCl_2$; (8) 50, $MgCl_2$*. Coagulation and flocculation took place almost immediately in the solution to whose symbols an asterisk is attached, but nothing (or at most only a slight increase in turbidity) occurred in the other cases. These results were discussed in detail by the speaker with reference to the principles involved.

coloring, and of the manufacture of photographic materials and of modern explosives have to deal primarily with substances in this peculiar state of aggregation; that the clarification of syrups and other liquors and that of water and sewage by precipitation are based on the phenomena of absorption by colloidal substances; that it is with these substances as constituents of living bodies that physiology is mainly concerned; that they constitute the culture-media of the bacteriologist, to the employment of which the development of his science is largely due; and that to the geologist the phenomenon of the sedimentation of mud and slimes, which is closely related to that of the coagulation of colloidal suspensions, is one of much interest.

With these brief indications of the importance of the subject, I must now conclude this very inadequate survey of it. It remains only for me to express to you my thanks for your kind attention.

NOTE ON THE EFFICIENCY OF CENTRIFUGAL PURIFICATION.

By Theodore William Richards.

Received December 14, 1904.

For many years the advantages of centrifugal separation of mother liquor from crystals have been realized by technical chemists in the preparation and drying of sugar and many other substances. Probably also the washing of these substances during rapid rotation has been practiced by many. Certainly both these operations have frequently been used in this laboratory for the preparation of the pure substances necessary in precise work. Nevertheless, there is known to me no quantitative study of the efficiency of these processes; hence a short note concerning a brief series of experiments (made in the first place merely to determine the grade of purity which was probably being attained in a special series of consecutive recrystallizations) may be of service.

In the following tests, sodium nitrate was selected as a typical substance, and to it was added an impurity (nitric acid) whose quantity could easily be estimated. Sodium nitrate was chosen

because a little over half of the dissolved salt may easily be reclaimed by cooling,—an average yield—and the crystals are not of the needle or plate-like forms which commonly retain much mother liquor. Hence they would indicate a minimum, rather than a maximum, advantage in centrifugal action.

For the first series of experiments, 450 grams of this salt were dissolved in 220 grams of boiling water, and to the solution was added 15 grams of nitric acid (sp. gr. 1.40). Thus the original mixture was a solution of the salt with about 2 per cent. of impurity. It remained to determine how effectually the impurity could be removed by centrifugal separation.

The mixture was allowed to crystallize, 240 grams of salt separating out. The resulting mother liquor was about half normal in nitric acid. Upon draining it off by gravitation alone from the crystals, and shaking them together several times, about 3.5 to 4 cc. of this mother liquor were found to be retained by 10 grams of crystals. This volume corresponds to about 0.1 gram of nitric acid. The crystals thus now retained 1 per cent. impurity. With the help of a filter-pump and punctured diaphragm about half of this was removed, leaving still 0.5 per cent. of impurity.

The crystals were now transferred in bulk to the porcelain basket of a centrifugal machine. This basket had a radius of 65 millimeters, and could be rotated 2000 times in a minute. It was found that two minutes whirling or 4000 revolutions removed two-thirds of the residual mother liquor; and after washing with 0.025 liter of water, while rotating, somewhat over two-thirds of the remainder were removed.

The last mentioned portions of 10 grams (the weight of crystals removed for each test) thus contained only 0.005 gram of nitric acid, 0.05 per cent.) or only a twentieth of the amount which was retained when the mother liquor was merely allowed to drain by gravitation.

The crystals remaining were once more washed while whirling with a little water and dissolved in the least possible amount of boiling water and recrystallized. The mother liquor thus resulting was only 1/300 normal in nitric acid, or a hundred and fifty times as dilute as the previous mother liquor. Upon whirling the crystals for two minutes 10 grams of them were found to retain as before about 0.5 cc. of mother liquor, this time corresponding to 0.0001 gram of nitric acid or 0.001 per cent. Another slight

washing while in rotation removed nine-tenths of this acid, leaving only about 0.00001 gram of nitric acid in 10 grams of salt. This impurity of only 0.0001 per cent., or one part in a million, which needed delicate indication and titration in order to be detected at all, would be injurious in only very few cases.

Thus two crystallizations, each followed by centrifugal separation and a little centrifugal washing, had removed 19999/20000 of the impurity, leaving the salt practically pure.

The comparison of this procedure with the simple process of gravitational draining is instructive. Two crystallizations, followed merely by draining, would have removed only about nine-tenths of the impurity, since only about two-thirds of the mother-liquor can be thus decanted. Two more recrystallizations would have removed nine tenths of the residue, and two more, nine-tenths of that. Thus after six recrystallizations the remaining crystals would still have retained 0.002 per cent. of nitric acid or twenty times as much as was left after the *two* centrifugal treatments. Three *more*, or in all nine successive recrystallizations, would have been needed to attain this latter degree of purity; and any one having had experience with this operation can imagine the small residue which would then remain. If as much as half of the substance was recovered each time,[1] 0.2 per cent. or about 2 grams would remain as the total product from a kilogram after nine recrystallizations, whereas the yields after centrifugal treatments, each time washing with 50 cc. of water, would be 500 grams — 44 grams[1] = 456 grams after the first treatment, and one-half of 456 grams — 44 grams = 184 grams after two treatments.

In the first test much of the material was used in the successive analyses, hence a new series of two crystallizations was made. The yield and degree of purity corresponded satisfactorily with the preceding calculations.

In short, in the case of sodium nitrate, with two crystallizations, the salt obtained with the help of centrifugal separations and centrifugal washings is two thousand times as pure as that obtained merely by gravitational drainings; and for the attainment of an equal degree of purity the yield is about a hundred times as good by the centrifugal process, as it is by the draining process. The saving of time and labor is obviously very great.

[1] The solubility of sodium nitrate at 20° is 44 grams in 0.050 liter of water.

Of course these approximate figures, based upon actual experiment concerning a single salt, will not apply exactly in all cases. The size and form of the crystals, the percentage of salt recovered during each crystallization, the solid solution of isomorphous substances, inclusion, adsorption, the time and centrifugal intensity of the draining, and other circumstances, will effect the results. Nevertheless the general principle must apply in all cases. When the crystals are needle-shaped or when the solubility is very great, the gain in efficiency may be even greater, as was shown in an experiment with sodium chromate, $Na_2CrO_4.4H_2O$. This salt, crystallizing in long prisms, was found to gain over twice as much advantage as sodium nitrate from centrifugal treatment.

The analyses of the figures given above shows the great saving of time and efficiency to be gained by centrifugal washing alone. In these tests two-thirds to nine-tenths of the adhering mother liquor were in each case removed with a minimum of labor and very little loss of substance. The washing was conducted by simply allowing a fine stream of cold water blown from a wash bottle to play upon the rapidly rotating substance for a minute or two. This accomplished as much as two or three successive recrystallizations would have done without centrifugal action.

The process of centrifugal washing seemed worthy of a special test. Accordingly, 200 grams of fine crystals of sodium nitrate crystallized from an acid mother liquor were sprayed by degrees with 0.2 liter of water, the outflowing solution being tested from time to time.

The efficiency of the washing progressed with great regularity until about 0.15 liter of water had been used. This amount dissolved about 40 per cent. of salt and the washings of the salt were at this time less than a hundredth as acid as the original mother liquor. Further washing seemed to diminish the acidity but little, probably on account of the mother liquor included in cells in the crystals, hence the limit had been reached, and another crystallization must be made to attain greater purity.

Since 60 per cent. of the salt (120 grams) remained after this treatment, containing only 1 per cent. of the impurity which would have adhered to it without the centrifugal washing, it is clear that this process is a highly advantageous one. It is not, however, the most advantageous, there being two practical disadvantages in its action. One of these is the danger of uneven spraying, and the other the likelihood that even with the most even

distribution of the water some of the interstices between crystals might be untouched. Moreover, time is needed for mixing the impurity with the wash-water. These possibilities were very kindly pointed out to me by Dr. W. A. Noyes, who suggested that it might be more certain and effective to stop the centrifugal machine several times and stir the crystals each time with a small quantity of washing fluid. Accordingly, upon his suggestion, this procedure was tested. Because in the foregoing experiment the superficially clinging mother liquor was hard to distinguish from that included in cells within the crystals, the procedure was somewhat altered in this new trial.

In order to test the efficiency of the washing alone, crystals obtained from a *neutral* solution were thoroughly moistened with a normal acid solution and equal portions were tested by each of the two methods. The method suggested by Noyes proved itself to be the most efficient and trustworthy, in every case greatly exceeding the spraying process in effectiveness. For example, in one experiment 250 grams of fairly large crystals of sodium nitrate were stirred with 0.057 liter of normal nitric acid, enough to dissolve just 50 grams. The 200 grams of crystals remaining were whirled and then carefully stirred into 45 cc. of water—enough to moisten them thoroughly. After another whirling, two-thirds as much more water was stirred in, and after yet another whirling, 25 cc. more. Upon finally separating the mixture by centrifugal action, the residue of 110 grams of crystals was found to contain only a barely perceptible trace of acid. The three wash waters, each collected after thoroughly cleansing the apparatus, were respectively 0.06 normal, 0.006 normal, and 0.0004 normal. Thus the mother liquor had been diluted the first time to one-sixteenth its original strength, the residual liquid had been diluted again to one-tenth of that, and finally the last wash water effected a further diminution to one-fifteenth of the previous washing. Similar tests using the same amount of water continuously always left a larger yield of crystals, because the outflowing solution was not saturated, but never produced so pure a substance. Indeed, in one case the salt continuously washed contained fifty times as much acid as that found in the experiment detailed above, and with careless treatment the residual impurity might be even much greater. Similar confirmatory experiments were made with finely divided sodium chloride, with similar results.

Obviously, then, this method of washing by repeated stirring with small quantities of water and subsequent centrifugal treatment is higly efficient. The extent to which it may replace repeated crystallizations must vary so much in individual cases, with the ratio between the superficially and the internally imprisoned impurity, as to make exact calculations difficult; but in most cases it would probably be best to wash twice with small portions of water (enough to give the crystalline mass a pasty consistency) between each recrystallization.

Obviously the reason why centrifugal washing is so efficacious is simply because as much as possible of the preceding impure solution is removed before a new portion of wash water is added, hence a small amount of water will accomplish great dilution of the impurity.

From these remarks, it is clear that any one having a pure substance to prepare in large quantities would do well to find out how he could best combine in his particular case centrifugal washing with repeated crystallization in order to obtain a maximum output with the least labor and waste.

The application of centrifugal separation and washing need not be confined to a preparation on a large scale, however. The organic chemist has often a minute amount of a pure substance whose economical purification may be of the utmost significance to him. The principles in question apply just as well to such cases as to the manufacturer.

For manipulating very small quantities I have found it convenient to use a small centrifugal machine with aluminum containing tubes hinged upon a rapidly rotating axle, of the type so much used by technical analysts to hasten the separation of precipitates. Into the aluminum tubes are placed glass tubes suitable for containing the crystals to be freed from impurity. Several shapes may be used for these glass tubes, but the three forms shown (Figs. 1, 2 and 3) are especially convenient. In order to hold the crystals during the centrifugal separation either the containing tube is narrowed (Fig. 1) or a diaphram or bulb is placed across it (Fig. 2), about one-third of the distance from the bottom. In order that the mother liquor may be removed by suction without disturbing the crystals, a fine glass tube should be in-

Fig. 1.

Fig. 2.

serted as far as the bottom of the receptacle. This protruding tube should be bent or inclined to one side so as to interfere as little as possible with the filling. The two opposite arms of the centrifuge should of course be equally weighted. The single tube may be replaced by two tubes, as shown in Fig. 3. This last arrangement is in some respects the most convenient of all.

Fig. 3.

Yet another form of apparatus has been frequently used here, in work upon atomic weights. This apparatus may be described for the benefit of those unable to obtain the forms described above, because it is extremely inexpensive, and may be made by any one (see Fig. 4). Fig. 4 is three-sixteenths regular size. It was based on a form used by Professor Landolt long ago, although not resembling this in detail. A very stout large test-tube, intended to hold the crystals, was provided with a fine exit tube at the bottom; this exit tube was passed through the doubly-bored stopper of a smaller test-tube, designed to hold the separated mother liquor. A small platinum cone or bead supported the crystals. Each test-tube was provided with a bucket-like handle of stout wire, of copper or better of platinum, the wire from the smaller tube being firmly fastened to that around the neck of the larger one. To the larger wire-handle was attached a strong leather strap, or very stout closely woven cord, about 75 cm. long, by means of which the apparatus was whirled in the air as rapidly as possible in a circle nearly two meters in diameter. The radial support must be very strong, and not easily cut or frayed, because the strain is great. In our most accurate work, a platinum funnel has replaced the larger glass tube as a support for the crystals. This apparatus must be used only in an empty room, with great caution, since the strap may break, and might give rise to serious injury. On the whole, however, the gain from this extremely efficient apparatus has in our hands exceeded greatly the loss caused by its occasional destruction. Nevertheless, if obtainable, the rapidly revolving basket of porcelain or platinum, or the test-tube centrifuge, with aluminum guard-tubes so firmly mounted as to preclude disruption, is to be preferred on the score of safety.

Fig. 4.

In brief, the contents of the present note may be summarized as

follows: The very great gain in time, labor and material effected by centrifugal draining and washing during the purification of crystals is demonstrated by quantitative experiments, and simple forms of apparatus are suggested which secure these advantages to the organic chemist or to the worker with small quantities of precious material.

THE WATER OF THE YUKON.

By F. W. Clarke.

Received December 7, 1904.

Analyses of river waters are commonly made with reference to one or another of three distinct purposes, which we may call, respectively, the technical, the geological, and the sanitary. To the geologist, who requires a complete determination of the inorganic contents of a water, the data are interesting in so far as they help to elucidate the problem of "chemical denudation"; that is, to show how much material is removed from the surface of the land, and transported to the sea. On this subject much has been written, but the conclusions have been drawn from incomplete or defective evidence, as I shall show in a future publication. The present note is merely an addition to the list of available analyses, and it relates to a region for which, hitherto, no data existed.

On June 14, 1904, Mr. F. L. Hess, of the U. S. Geological Survey, collected, at my request, a sample of water from the Yukon River. The sample was taken in midstream, above the town of Eagle, a little below north latitude 65°, and nearly on the boundary between Alaska and Canada. It was fairly but not absolutely clear, and contained 0.1565 gram of suspended, inorganic sediment, as weighed after ignition. The soluble, inorganic constituents of the water are given in the subjoined analysis by Mr. George Steiger, and there was also some organic matter undetermined. The CO_3 represents normal carbonates only, in order that the water may be compared with others which are stated in similar terms; the silica and alumina are conventionally reported as present in colloidal form.

	Parts per million.	Percentage of total solids. A. Yukon.	B. St. Lawrence.	C. Rhine.	D. Baikal.
CO_3	45.1	46.16	44.43	47.06	49.85
SO_4	10.5	10.75	11.17	12.61	6.93
Cl	0.4	0.41	2.41	4.17	2.44
NO_3	....	.....	.....	.....	0.21
PO_4	....	.....	.....	0.28	0.72
Ca	21.7	22.21	20.67	27.36	23.42
Mg	4.6	4.71	6.44	5.57	3.57
Na	6.0	6.14	4.87	2.69	5.85
K	trace	trace	.....		3.44
NH_4	....	.....	.....	.....	0.08
SiO_2	7.6	7.78	10.01	0.17	2.03
Al_2O_3	1.8	1.84	.....	0.09	1.46
Fe_2O_3	....	.....	.....		.....
	97.7	100.00	100.00	100.00	100.00
Salinity in parts per million		97.7	148.0	178.0	69.0

The CO_2 "half combined" in the Yukon water is 20.5 parts per million.

The columns which give the percentage composition of the mineral matter dissolved in the river water, are peculiarly useful. They enable us to compare different waters with one another independently of the great variations which they exhibit in respect to dilution. Out of a large number of analyses of river and lake waters, which I have reduced to uniform standards, the following approximate most nearly to the Yukon.

B.—The Saint Lawrence, opposite Montreal. Analysis by Norman Tate. The high silica is due in part to the influence of the Ottawa, and the chlorine may represent pollution.

C.—The Rhine, at Cologne. Average of four analyses by Vohl. The high chlorine is again noticeable.

D.—Lake Baikal, Siberia. Analysis by Schmidt.

The Yukon, then, at least where the sample was taken, is a fairly typical calcium carbonate water, with a remarkably low proportion of chlorides. It belongs to a large and well-defined group of natural waters, and it is desirable that other rivers of the far north should be examined for comparison with it. Such rivers probably represent the minimum of contamination through human agency, and their composition is therefore particularly significant for geological discussion. Rivers, however, vary in composition from time to time and place to place, and a single analysis does

not give all the information that is needed. I hope that later samples from other points on the Yukon may be available for analysis, in order that its possible variations may be discovered and recorded.

U. S. GEOLOGICAL SURVEY, WASHINGTON,
December 5, 1904.

THE WATER OF UTAH LAKE.[1]

BY F. K. CAMERON.

Received November 29, 1904.

IN looking over the analyses of waters from several lakes and streams with Professor F. W. Clarke, the writer's attention was called to the great discrepancy between an unpublished analysis of water from Utah Lake made in the laboratory of the Bureau of Soils in 1903 and one made by Clarke twenty years earlier.[2] Further, neither of these analyses agree with one of a sample of water taken from the Jordan River at the outlet of the lake, made by the writer in 1899.[3] The results of these analyses are given below:

ANALYSES OF UTAH LAKE WATER.

Results stated in parts per million of solution.

	U. S. Geol. Survey.	Bureau of soils.	
	Clarke.	Cameron.	Brown.
	1883.	1899.	1903.
Ca	55.8	67.6	80.0
Mg	18.6	13.8	92.0
Na	17.7	233.7	247.0
K	?	?	30.0
SO_4	130.6	236.7	365.0
Cl	12.4	316.5	336.0
HCO_3	.....	.....	266.0
CO_3	60.9	23.7	.....
SiO_2	10.0	.....	.....
	306.0	892.0	1416.0

These figures show that the total salt content has increased very markedly since 1883, the greatest increase being in the sodium and the chlorine. In order to confirm this interesting observation, the Bureau has had a number of other samples collected at different points in the lake and analyzed. These samples were collected by

[1] Published by permission of the Secretary of Agriculture.

[2] U. S. Geological Survey, Bull. No. 9, p. 99 (1884).

[3] Field Operations of the Division of Soils, 1899, p. 108.

Mr. W. H. Heileman on May 18, 1904. At this time the level of the lake was somewhat higher than usual, the surface being about two feet below "Compromise Point," and the water was slightly murky. The temperature of the lake water was about 65° F. One large sample of the lake water itself was taken, and two smaller ones from above springs in the bottom of the lake. The samples were as follows:

Sample No. 1 was taken from the center of Section 31, Range 1 East, Township 5 South. It was about one and a half miles from the North shore line, away from any inlet or other source of unfairness in sampling. It was taken 5 feet below the surface of the water, the depth at this point being 8 feet.

Samples Nos. 2 and 3 were taken above springs in the lake one and a quarter miles from where Sample No. 1 was taken. Their location is in Section 25, Range 1 West, Township 5 South. These two springs issue from the bed of the lake and the water over the crater of these springs is very deep. The cavities from which the springs pour into the lake are perhaps 200 feet in diameter. The water from the springs is warm, does not freeze in winter and much vapor or "steam" rises continually over the springs in cold weather. No. 2 was taken from the eastern spring at a depth of 12 feet, No. 3 from the western spring at a depth of 15 feet.

Sample No. 4 was collected on August 31, 1904, by Mr. Heileman. The level of the lake was still somewhat higher than is normal for the season of the year. This sample was taken off shore about one and a half miles from the town of Provo, Utah, at a depth of 3 feet, the lake itself being six feet in depth at this point. There were no inlets to the lake in the vicinity where the sample was taken.

The analyses of Samples Nos. 1, 2 and 3 were made by Dr. Atherton Seidell. A complete analysis of Sample No. 1 was made. Neither phosphates nor nitrates were recognized in repeated tests for them. In Samples No. 2 and 3 only the more important constituents present were determined and no attempt made to estimate rare alkalies or alkaline earths. Total solids by the evaporation of Sample No. 1 gave 1200 parts per million. Suspended matter in Sample No. 1 was 51 parts per million, and for samples Nos. 2 and 3, 53 parts per million. Sample No. 4 and the sample obtained in 1903 were analyzed by Mr. Bailey E. Brown, only the more important constituents being determined.

The analyses of these four samples of water from Utah Lake are given in the following table:

ANALYSES OF UTAH LAKE WATER.
Results stated in parts per million of solution.

	1.	2.	3.	4.
Ca	67.7	68.0	70.5	67.0
Sr	1.7	.....	.....	.....
Mg	73.5	71.5	71.0	86.0
Na	207.2	218.3	210.5	230.0
K	25.8	24.3	25.7	22.0
Li	0.7	.....	.....	.....
SO_4	332.9	330.4	324.4	378.0
Cl	288.5	288.5	288.5	337.0
HCO_3	205.5	266.0	260.0	194.0
CO_3	24.0	trace	trace	11.0
SiO_2	22.6	24.5	22.7	28.0
	1250.1	1291.5	1273.3	1353.0

It is at once apparent from the results that the analysis of 1903 is substantiated, and that the great discrepancies with the analysis of Clarke, in 1883, as well as with that of the writer, in 1899, are due to actual changes in the lake water itself. The greatest increase is in the sodium and the chlorine, and it is probably due to the sodium chloride in the seepage waters from the irrigated lands adjoining the lake. The probable causes of the increased total salt content of the lake water are: The influence of seepage water from the surrounding irrigated lands which have been brought under cultivation since the analysis of Clarke was made; the diversion of fresh streams for irrigation purposes, which streams formerly flowed directly into the lake; and the relatively large effects produced by evaporation in so shallow a body of water. An examination of the figures further shows that the composition of the waters taken from above the crater of the springs is not materially different in composition from that of the lake water taken elsewhere. Since the samples, however, were taken only at a moderate depth as compared with the depth of the craters it does not follow that the analyses represent the true composition of the spring waters themselves. Concerning these springs, Mr. Heileman writes:

"Recent surveys and explorations show that while there is little water entering the lake from streams, there is a great inflow continually from the springs issuing from the bed of the lake. The spring water is in part cold. There are also several hot springs

issuing from the bed of the lake along its west shore line. One in particular has been explored which issues from a crater or sink 100 feet deep with a diameter of several hundred feet. The water delivered forms an important part of the present lake supply. A pipe lowered into the cavity caused the water to rise in the pipe above the lake surface. This water was too hot to permit coming in contact with the hands without seriously scalding or burning."

It is hoped that there will be an opportunity of securing the material necessary to make a comparison of the spring water with that of the lake.

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U. S. DEPARTMENT OF AGRICULTURE,
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[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, NO. 102.]

THE APPLICATION OF BISMUTH AMMONIUM MOLYBDATE TO GRAVIMETRIC ANALYSIS.[1]

BY EDMUND H. MILLER AND FREDERICK VAN DYKE CRUSER.

Received December 9, 1904.

BISMUTH may be determined volumetrically by the titration of reduced molybdenum from bismuth ammonium molybdate, which is precipitated in a barely acid solution by ammonium molybdate.[2] It was suggested by Dr. W. A. Noyes that the precipitate of bismuth ammonium molybdate might be ignited and the combined oxides weighed.

Therefore, this work was undertaken in order to determine whether this method could be made sufficiently accurate to be used as a method for the determination of bismuth, and to determine how it compares with the volumetric method.

EXPERIMENTAL.

A bismuth nitrate solution was made up, containing about 19 grams of the crystallized salt per liter, and 45 grams of free nitric acid; also a large amount of ammonium sulphate solution and ammonium nitrate solution (each 30 grams of the crystallized salt per liter). The bismuth nitrate solution was first standard-

[1] Read at the meeting of the New York Section of the American Chemical Society, January 6, 1905.

[2] Riederer: This Journal, **25**, 907 (1903).

ized, and as the subsequent results depended upon the accuracy in the determination of the bismuth content of the solution, several methods were pursued in order to find the exact percentage of bismuth present.

First, different quantities of the bismuth solution were taken, a few drops of concentrated nitric acid added to each, and the solutions evaporated to dryness on the water-bath in weighed platinum milk dishes. These were then heated in an air-bath at 120° C., and finally ignited and weighed. It was noticed that the oxide was brown in color and that it melted. The results are given below:

Bismuth solution taken. cc.	Weight of bismuth trioxide found. Gram.	Weight of bismuth found. Gram.	Weight of bismuth per cubic centimeter. Gram.
15	0.1336	0.1198	0.007987
20	0.1783	0.1599	0.007995
20	0.1784	0.1600	0.007999
25	0.2225	0.1995	0.007984
30	0.2670	0.2394	0.007981
35	0.3127	0.2795	0.007987
		Average,	0.007989

Two of these residues were again dissolved in a few drops of nitric acid, evaporated to dryness at 160° C. in an air-bath, and heated in a muffle-furnace, giving slightly higher results.

The bismuth solution was next standardized by precipitating the bismuth as basic carbonate by the addition of ammonia and ammonium carbonate, and filtering on a platinum Gooch crucible, washing with cold water. When thoroughly washed, the precipitate was ignited to oxide and weighed, giving the following results:

Bismuth solution taken. cc.	Weight of bismuth trioxide found. Gram.	Weight of bismuth found. Gram.	Weight of bismuth per cubic centimeter. Gram.
15	0.1345	0.1206	0.008041
20	0.1791	0.1606	0.008031
		Average,	0.008036

Different amounts of the bismuth solution were precipitated by ammonia and ammonium carbonate as before, but filtered on ashless papers, dried, the precipitate separated from the paper, the paper moistened with nitric acid and burned in a weighed porcelain crucible, the bulk of the precipitate added and ignited to oxide with nitric acid.

Bismuth solution taken. cc.	Weight of bismuth trioxide found. Gram.	Weight of bismuth found. Gram.	Weight of bismuth per cubic centimeter. Gram.
15	0.1320	0.1184	0.007892
20	0.1746	0.1566	0.007829
25	0.2211	0.1983	0.007931
		Average,	0.007884

From these results we can readily see that some bismuth is lost, although the precipitates were treated very carefully.

The results obtained by weighing the ignited basic carbonate in a platinum Gooch crucible being somewhat higher than those obtained by evaporation and ignition in platinum, it was thought that these low results were due to a slight reduction by unburned gases, probably hydrogen, passing through the bottom of the platinum dish. Therefore, different amounts of the bismuth solution were evaporated to dryness in large porcelain crucibles, dried at 160° C. in an air-bath and ignited. The oxide obtained was canary-yellow in color.

Bismuth solution taken. cc.	Weight of bismuth trioxide found. Gram.	Weight of bismuth found. Gram.	Weight of bismuth per cubic centimeter. Gram.
20	0.1793	0.1608	0.008039
25	0.2238	0.2007	0.008028
30.025	0.2692	0.2414	0.008047
		Average,	0.008038

This value for bismuth corresponds with that obtained by the basic carbonate ignition in a platinum Gooch crucible, and, therefore, 0.008037 gram bismuth per cubic centimeter was taken as the correct value of the solution.

To find whether bismuth ammonium molybdate may be ignited and the bismuth thus determined from the oxides $Bi_2O_3.4MoO_3$, different quantities of the bismuth nitrate solution were precipitated according to the method of Riederer,[1] washing one series with ammonium sulphate and another with ammonium nitrate. The precipitates were filtered by suction on a platinum Gooch crucible, and washed with from 300 to 400 cc. of these solutions. When washed, the precipitates were dried by standing the crucibles on an asbestos plate on a stove and then heated inside of an iron crucible, having the bottom red hot. The caps of the Gooch crucibles were put on and the precipitates moistened with a few drops of concentrated nitric acid and ignited, being careful

[1] This Journal, **25**, 907 (1903).

to keep the bottom of the platinum crucible not above a dull red heat. The precipitates were again moistened and heated. This was continued until the color of the precipitates was a very light yellow. The crucibles were then allowed to cool in a desiccator and weighed. The weight of bismuth was then calculated, the factor being 0.40058. Results by washing with ammonium sulphate:

Bismuth solution taken. cc.	Weight of precipitate found. Gram.	Weight of bismuth found. Gram.	Weight of bismuth taken. Gram.
10	0.2020	0.0809	0.08037
20	0.4010	0.1606	0.16074
20	0.4033	0.1616	0.16074
25	0.4988	0.1998	0.20092
30	0.6102	0.2443	0.24111

Results by washing with ammonium nitrate:

Bismuth solution taken. cc.	Weight of precipitate found. Gram.	Weight of bismuth found. Gram.	Weight of bismuth taken. Gram.
20	0.3935	0.1576	0.16074
20	0.3967	0.1589	0.16074
25	0.4896	0.1961	0.20092
25	0.4992	0.2000	0.20092
30	0.5988	0.2399	0.24111
30	0.5998	0.2403	0.24111

The first and third in the second series were slightly too acid, giving incomplete precipitation and low results.

Different amounts of the bismuth solution were then precipitated by the method of Miller and Frank.[1] The precipitates were filtered on a platinum Gooch crucible and treated as before.

Results by washing with ammonium sulphate:

Bismuth solution taken. cc.	Weight of precipitate found. Gram.	Weight of bismuth found. Gram.	Weight of bismuth taken. Gram.
10	0.2003	0.0802	0.08037
10	0.2025	0.0811	0.08037
15	0.3028	0.1213	0.12056
20	0.4057	0.1625	0.16074
20	0.4034	0.1616	0.16074

The first precipitate, after the final weighing, was heated for twelve minutes with a good full flame of a Bunsen burner and lost 0.0038 gram; then with the same flame for thirty-eight minutes and lost 0.0029 gram; then for one hour and twenty-five minutes, losing 0.0031 gram; and when heated with a blast lamp

[1] This Journal, **25**, 926 (1903).

for five minutes the loss was 0.0050 gram, showing that the igniting of the precipitate must be done very carefully.

Results by washing with ammonium nitrate:

Bismuth solution taken.	Weight of precipitate found.	Weight of bismuth found.	Weight of bismuth taken.
5	0.0994	0.0398	0.04018
10	0.2013	0.0806	0.08037
15	0.3011	0.1206	0.12056
20	0.3992	0.1599	0.16074
25	0.4985	0.1997	0.20092
30	0.6024	0.2413	0.24111
35	0.6995	0.2802	0.28129

From the above results we can see that the most accurate results are obtained by using the precipitation method of Miller and Frank,[1] washing with ammonium nitrate. These conditions, in detail, are as follows: To the bismuth nitrate solution ordinary acid ammonium molybdate is added in excess (four to five times the amount necessary for precipitation), no precipitate being formed at this point. Then a few drops of congo red are added, and very dilute ammonia from a burette, stirring all the time. The ammonia is added until the solution becomes pink, and then a drop or two of dilute nitric acid till the color is lilac. The bulk of the solution is then made up to 150 to 200 cc., and heated slowly on a stove, stirring once in a while. When the solution has reached a temperature between 50° and 60° C. it is filtered on a platinum Gooch crucible and washed with a 3 per cent. solution of ammonium nitrate until the bulk of the filtrate has reached from 400 to 500 cc. Then the crucible with its cap is placed in an air-bath and dried at 160° C. When thoroughly dry it is moistened with a few drops of concentrated nitric acid and heated at the tip of the flame of a Bunsen burner, being careful to prevent the bottom from becoming more than dull red. It is again moistened with concentrated nitric acid, ignited, and this continued until the precipitate is very light yellow in color, when its weight will become constant.

In order to compare this method with the volumetric method, different amounts of the bismuth nitrate solution were precipitated and the bismuth determined according to the method of Miller and Frank,[1] the same conditions being followed, and the solution being titrated according to their experiment, II.

[1] This Journal, **25**, 926 (1903).

Bismuth solution taken. cc.	Potassium permanganate required. cc.	Weight of bismuth found. Gram.	Weight of bismuth taken. Gram.
15	26.95	0.1207	0.12056
15	26.9	0.1205	0.12056
20	35.7	0.1599	0.16074
20	36.15	0.1619	0.16074
25	45.35	0.2031	0.20092
25	45.25	0.2027	0.20092

This shows that the results obtained by the gravimetric method are as accurate as those found by the volumetric procedure.

CONCLUSIONS.

(1) To determine bismuth by the evaporation of a nitric acid solution of bismuth nitrate the operation must be conducted in porcelain, otherwise some bismuth trioxide is reduced.

(2) In the precipitation of ammonium bismuth molybdate the use of congo red is preferable to methyl orange, and in washing the precipitate ammonium nitrate is better than ammonium sulphate.

(3) Bismuth may be determined correctly by the ignition of bismuth ammonium molybdate to $Bi_2O_3.4MoO_3$ when the temperature of ignition is kept below a dull red heat.

QUANTITATIVE LABORATORY,
COLUMBIA UNIVERSITY,
December 3, 1904.

COLORIMETRIC DETERMINATION OF PHOSPHORUS.

BY THOMAS E. HEWITT.

Received November 26, 1904.

THE color given on passing hydrogen sulphide into an alkaline molybdate solution seemed favorable for a colorimetric determination of molybdenum, and indirectly of phosphorus. The following method has been developed on this basis:

Standard Molybdic Acid Solution.—One cc. = 0.004108 gram MoO_3, equivalent to 0.000073 gram phosphorus.

Standard Phosphomolybdate Solution.—One cc. = 0.000006+ gram of phosphorus, 5 cc. = 0.419 cc. of the standard molybdic acid solution; prepared by dissolving ammonium phosphomolybdate in about the theoretical amount of sodium hydroxide.

In the following experiments 12-ounce bottles, 2 inches square, were used. The standard solution was placed in the bottle filled

half full with water and hydrogen sulphide was passed until the solution was saturated, then the bottle was filled to the neck.

It was found, after numerous experiments, using different quantities of molybdic acid solution and equivalent quantities of the phosphomolybdate solution, that a darker color was obtained with phosphomolybdate, thus making it necessary to use a standard comparison solution of phosphomolybdate. Equal quantities of phosphomolybdate always give the same color.

Sodium hydroxide in reasonable excess of the amount necessary to dissolve a given precipitate is not detrimental to the results. A blackish solution will be given, if too little sodium hydroxide is used.

The solution must be saturated with hydrogen sulphide, as too little will give a light colored solution. The right color, after treating with hydrogen sulphide, is yellowish red. Saturation can be obtained by passing the gas at a moderate rate for five minutes.

The solutions when treated are not affected by air, but gradually darken on standing as the reactions involved progress. By heating the sulphuretted solution in boiling water for five minutes the color assumes a shade permanent for two hours.

Using Nessler tubes of 16 mm. bore and a depth of liquid of 24.5 cc. it was possible to detect a difference of 0.00000089 gram phosphorus.

METHOD.

Weigh off 2 grams of pig iron, or steel, or the substance to be tested, dissolve and obtain the precipitate of phosphomolybdate as in any other volumetric determination of phosphorus. Collect the precipitate on a 9 cm. filter and wash with 2 per cent. nitric acid. Place the funnel with the precipitate in the neck of a 100 cc. measuring flask, churn with hot water and add N/10 NaOH until the precipitate is dissolved. Do not use stronger sodium hydroxide, as there is danger of too large an excess, since there is only a small quantity of phosphomolybdate. Add the hot water first to protect the filter. If the filter is broken, shreds will pass into the solution and interfere with the reading. Read the burette containing the N/10 NaOH and add one-half of the amount of sodium hydroxide necessary to dissolve in excess. Fill to the mark. Take an aliquot part and place in a 50 cc. Nessler tube, fill half full with water and pass hydrogen sulphide

at a moderate rate for five minutes, then place into boiling water and let stand for five minutes; remove, fill to the mark and compare with the standard, which is made by placing 10 cc. of the standard phosphomolybdate solution in a Nessler tube, filling half full with water and passing hydrogen sulphide for five minutes, heating for five minutes in boiling water and then filling to the mark. Compare the colors by looking down through the tubes, having light reflected upwards.

Standard Phosphomolybdate Solution.—The yellow precipitate was obtained in bulk by precipitating sodium phosphate with ammonium molybdate, thoroughly washing the precipitate with 2 per cent. nitric acid and drying in a steam oven. Take 0.2737 gram of yellow precipitate, place in a 500 cc. measuring flask and add just enough N/10 NaOH for solution, then add one-half of the amount necessary for solution, in excess. Make up to 500 cc. Ten cc. = 0.000009122 gram of phosphorus. If the standard phosphomolybdate solution is stronger than here given, 10 cc. will give a color too dark for comparison. N/10 NaOH is made by dissolving 4 grams of pure sodium hydroxide and making up to 1000 cc. Its strength need not be determined further.

The following are phosphorus results obtained in pig iron and steel which Mr. Camp, of Carnegie Steel Co., and Mr. Glass, of LaBelle Steel Co., kindly furnished me:

	Phosphorus by titration with standard NaOH. Per cent.	Phosphorus by above method. Per cent.
Low phosphorus metal, 1	0.044	0.044
" " " 2	0.044	0.044+
" " " 3	0.044	0.044=
" " " 4	0.044	0.044+
" " " 5	0.044	0.044—
Bessemer pig iron, 1	0.081	0.084
" " " 2	0.081	0.086
" " " 3	0.081	0.083
Bessemer pig iron, 1	0.102	0.087
" " " 2	0.102	0.089
" " " 3	0.102	0.087
" " " 4	0.102	0.088
" " " 5	0.102	0.087--
Low phosphorus metal, 1	0.042	0.0419
" " " 2	0.042	0.0419
Bessemer pig iron, 1	0.088	0.079
" " " 2	0.088	0.081
" " " 3	0.088	0.083
" " " 4	0.088	0.081—

The phosphorus given above by titration is an average of from two to five results, done by the men at the works.

Standard phosphorus pig iron of Mr. Camp's.	Phosphorus by weighing yellow precipitate. Per cent.	Phosphorus by above method. Per cent.
1	0.109	0.108+
2	0.109	0.109—
3	0.109	0.109+
4	0.109	0.109+

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[CONTRIBUTION FROM THE HAVEMEYER LABORATORIES, COLUMBIA UNIVERSITY, No. 103.]

THE DETERMINATION OF AMMONIA IN MILK.

BY W. N. BERG AND H. C. SHERMAN.

Received November 28, 1904.

THE object of this work was to find a method sufficiently delicate for the determination of such small quantities of ammonia as exist in fresh milk, and in which the danger of splitting off ammonia from organic matter during the determination should be reduced to a minimum. Such a method would not only be useful in the study of certain types of fermentation, but would also probably yield results of value from a sanitary standpoint. Changes which result in a breaking-down of proteid matter are more likely to render milk unwholesome than those which affect only the milk sugar, and, while it is possible that some better index of proteid decomposition may be found, the determination of ammonia naturally suggests itself in this connection.

The method which appears to have been commonly used for the determination of ammonia in milk or cheese is to boil either the aqueous infusion of the sample or the filtrate from the precipitation of proteids with magnesium oxide or barium or sodium carbonate under atmospheric pressure, the liberated ammonia being caught in standard acid. Under these conditions urea gradually breaks down with the formation of ammonia. The ammonia which could be thus split off from the amount of urea probably present would doubtless be negligible as compared with the amounts ordinarily found in the analysis of cheese, but might entirely vitiate the determination of ammonia in fresh milk. In

our earlier experiments we made several attempts to determine the free ammonia in milk on the principle used in water analysis, but found that even when 1 cc. of milk was diluted with 1000 cc. of ammonia-free water and distilled under atmospheric pressure with only 0.1 gram of sodium carbonate more ammonia was always found in the distillate than previously existed in the milk.

After a number of unsuccessful experiments with other methods, in which magnesium oxide, as well as sodium carbonate, were tried, we concluded that accurate results can only be expected when the greatest possible care is taken to prevent the cleavage of ammonia from organic compounds, and that this can best be done by lowering the temperature at which the ammonia is expelled from the alkaline liquid. Folin's method,[1] in which the ammonia is removed from the solution by a rapid current of air in the cold, offers distinct theoretical advantages, but is hardly adaptable to the conditions of the ordinary analytical laboratory. The Boussingault-Shaffer method appeared to be equally efficient for the separation of ammonia from urea, and more promising for our present purpose. This method, developed by Shaffer[2] from the vacuum distillation process of Boussingault,[3] has been applied by the former to urine with very satisfactory results. With the modifications which we have found necessary or desirable in adapting it to milk it is as follows:

THE BOUSSINGAULT-SHAFFER METHOD MODIFIED FOR MILK.

Fifty cc. each of the milk sample and of neutral methyl alcohol are brought into a 2-liter round-bottomed flask with 10 grams of sodium chloride[4] and 0.5 gram of sodium carbonate.[5]

The flask is closed with a two-holed rubber stopper fitted with an inlet tube (to admit air at the end of the operation) and a Hopkins distilling head. By means of glass tubing the distilling head is connected with two absorption cylinders in series, and these in turn with a suction pump. On account of the tendency of the milk to froth during the distillation it is desirable to use a 2-liter flask when working with portions of 50 cc. If persistent

[1] *Ztschr. physiol. Chem*., 1902-3, **37**, 161.

[2] *Am. J. Physiol.*, 1903, **8**, 330.

[3] *Ann. chim. phys.*, 1850, **29**, 472; *J. prakt. Chem.*, 1850, **51**, 281.

[4] The sodium chloride was not always used. See paragraph on influence of sodium chloride below.

[5] If the milk is decidedly acid, determine the acidity and add 0.5 gram of sodium carbonate plus the amount required to neutralize the free acid present.

frothing occurs, it may be stopped by admitting a little air through the inlet tube. The absorption cylinders used were about 2.5 cm. in diameter and 20 cm. high, and together contained from 15 to 25 cc. of N/20 sulphuric acid, diluted with water to 40 cc. During the distillation these cylinders were surrounded by ice water. To guard against loss in case any liquid should be drawn out of these cylinders during the distillation, a clean suction bottle is interposed between the second cylinder and the pump. The general arrangement of apparatus was thus the same as that described and illustrated by Shaffer.[1]

The apparatus being tightly connected, the suction is started and the flask is lowered into a water-bath having a temperature of 60° to 65°. In a minute or two the mixture begins to boil briskly and the temperature of the bath may then be allowed to fall several degrees, the boiling-point depending, of course, upon the efficiency of the suction. In our work the pressure was usually about 50 mm. and the boiling-point ranged from 56° to 62°. The mixture was usually distilled for fifteen minutes, the operation being discontinued by turning off the suction and at the same time admitting air through the inlet tube, both done carefully, so that the acid in the absorption cylinders shall neither be forced out into the suction bottle nor back into the distillation flask.

The distillation being finished the apparatus is disconnected, the volume of distillate noted and the whole contents of the two absorption cylinders, the suction bottle and the connecting tubing, are rinsed into a beaker, diluted to 250 cc. and the excess of acid determined by titration with N/20 sodium hydroxide. Three drops of 0.5 per cent. solution of congo red were used as indicator in all of these titrations.

After each determination the distilling flask and the pipette used in measuring the milk were carefully cleaned with a solution of potassium dichromate in strong sulphuric acid, thoroughly washed until every trace of acid or curd was removed and then rinsed once or twice with distilled water practically free from ammonia.

Correction for Methyl Alcohol.—The methyl alcohol which collects in the absorption cylinders was found to have a very appreciable influence upon the end-point in the final titration, re-

[1] *Loc. cit.*

quiring a correction which should be varied according to the amount present in each case. This is the reason for noting the volume of distillate collected. Since the standard acid used for the absorption was always diluted to 40 cc., the total volume of liquid in cylinders (and suction bottle) at the end of the distillation shows the amount of distillate which has been caught. As the result of many blank experiments it was found that when the volume of distillate was from 30 to 39 cc. the alcohol present affected the end point to an extent equivalent to 0.4 cc. of N/20 alkali. The corresponding correction for 40-49 cc. of distillate was 0.5 cc. and for 50-60 cc. of distillate, 0.6 cc. In our regular determinations the volume of distillate was always between 30 and 60 cc.—usually between 45 and 55 cc.

Influence of Sodium Chloride.—Obviously the saturation of the boiling mixture with sodium chloride as recommended by Shaffer will lessen the hydrolytic dissociation of the sodium carbonate and thus render less likely the cleavage of ammonia from organic matter. On the other hand, the purest available sodium chloride contained sufficient ammonia to require a correction of 0.34 mg. or as much as was found in 50 cc. of some fresh milks distilled without the addition of the salt. In view of the fact that many of our samples contained so little ammonia and that those first tested gave no indication that the use of salt was necessary, it was omitted in all of our earlier work. Later it was found that while the presence of salt made little if any difference in the distillation of fresh milk, most of the older samples yielded appreciably less ammonia when saturated with salt before distillation.

The following cases are typical.

A sample of bottled milk purchased from one of the largest dealers in the city on July 7, 1904, and examined the same day, yielded with salt 0.00033 per cent. ammonia; without salt 0.00049 per cent. The difference corresponds to only 0.1 cc. N/20 alkali and is therefore within the limits of experimental error. Four days later the same milk, which had been kept in a refrigerator except for a short time each day, yielded as the result of concordant duplicates, 0.0059 per cent. ammonia with salt and 0.0093 per cent. without, the salt in this case making a difference equivalent to 2.0 cc. of the N/20 solution.

Bottled milk from another dealer analyzed within one day after delivery, yielded 0.0004 per cent. without and 0.0002 per

cent. with salt, the difference being again within the limits of experimental error.

Portions of two or three bottles of "certified" milk from a high-class dairy, after having been kept in a refrigerator for two to four days, were mixed and allowed to stand in an open bottle in a warm room. Within a day the milk curdled without developing a sour odor but with some evolution of gas. The bottle was allowed to stand for about a week, the curd and cream rising until over half of the liquid was a nearly clear whey. The cream became rancid and the curd developed a slightly "cheesy" but not unpleasant odor. The whey was filtered into a sterilized flask and kept in a cool room for five weeks without developing any unpleasant odor. This sample yielded 0.0038 per cent. ammonia when distilled without and 0.0028 per cent. when distilled with salt. Although the amount of ammonia which had developed in this sample was remarkably small, the influence of the salt is unmistakable.

A sample of milk of fair quality one day old was contaminated during handling with a few drops of old decomposed milk, and then kept at room temperature for about five months. Considerable gas was formed, and the acidity rose until 10 cc. neutralized 35.5 cc. of N/10 alkali, using phenolphthalein as indicator. The sample developed an odor suggesting sour kumyss and a very disagreeable bitter taste. It yielded 0.0175 per cent. ammonia with, and 0.0233 per cent. without salt.

Another portion of the same lot of milk was kept uncontaminated and was mixed with about 1 part formaldehyde to 1,000 parts of milk. This milk did not curdle until about four weeks old and only a moderate amount of gas was formed after curdling. The odor resembled that of sweet buttermilk. Though the formaldehyde prevented souring for several weeks, the acidity at the end of five months was three-fourths as high as in the preceding sample, 10 cc. neutralizing 27.3 cc. of N/10 alkali. This sample when five months old, yielded 0.021 per cent. ammonia, whether distilled with or without salt.

On the whole, then, it appears that with fresh milk it makes little if any difference whether or not the solution is saturated with salt before boiling with sodium carbonate. In other words, fresh milk contains little if any material which can be decomposed so as to liberate ammonia when treated with sodium carbonate under the conditions obtaining in the vacuum distillation method while milk which has been kept without a preservative and allowed to become stale does contain some such easily decomposable constituent, so that it is necessary to diminish the dissociation of the sodium carbonate if the true amount of free ammonia is

to be found by this method. The excess of ammonia found in the absence, over that found in the presence, of salt may conveniently be referred to as "cleavage ammonia," since it undoubtedly results from the cleavage of nitrogenous organic compounds.

So far as examined, all samples which had been kept for two days or more without a preservative contained appreciable amounts of cleavage ammonia," the quantity being, in general, roughly proportional to the degree of decomposition which had taken place in the milk. Whether the absence of "cleavage ammonia" in the sample preserved by formaldehyde is to be attributed to the further change of the unstable decomposition products into simpler and more stable forms, or to the influence of the preservative in checking the growth of those organisms to which the formation of the unstable compounds is due, cannot be stated with certainty until further observations have been made. The latter explanation appears, however, the more probable.

Evidently in the examination of samples of unknown history the use of salt to diminish the hydrolytic dissociation of the sodium carbonate should never be omitted if the true amount of free ammonia is desired. In many cases, however, it is believed that the amount of "cleavage ammonia" will throw important light upon the nature of the fermentation which has taken place. Moreover, since both "free" and "cleavage" ammonia increase as the milk becomes stale it is not improbable that the sum of the two—*i. e.*, the amount of ammonia yielded by distillation without salt—may be more useful than the true amount of free ammonia as a practical measure of proteid decomposition.

Check Experiments.—As a check upon the accuracy of the method above described a number of determinations were made with solutions containing known amounts of pure ammonium chloride. The following results were obtained:

Expt. No.	Ammonia taken. Gram.	Ammonia recovered. Gram.	Difference. Ammonia. Gram.	Equivalent to N/20 solution. cc.
1	0.0005 in water	0.00043	0.00007	0.08
2	0.0020 " "	0.00200	.....	.....
3	0.0040 " "	0.00393	0.00007	0.08
4	0.0060 " "	0.00597	0.00003	0.04
5	0.0080 " "	0.00809	0.00009	0.10
6	0.0120 " "	0.01195	0.00005	0.06
7	0.0020 in milk	0.00187	0.00013	0.15
8	0.0060 " "	0.00595	0.00005	0.06

While Shaffer used the method for the determination of much larger amounts of ammonia in urine, we prefer not to distil more than 10 or 12 mg. of ammonia in a determination. This corresponds to over 0.02 per cent. of ammonia, which would rarely be found except in very highly fermented samples. In such cases we prefer to use a smaller quantity of the sample diluted with water to 50 cc. The above check experiments, therefore, cover the range of all ordinary work, and allowing for the unavoidable errors of manipulation, it will be seen that the recovery of ammonia was quantitative in each case.

Since some of the samples used were preserved by means of formaldehyde (usually 1 part to 1000 of milk) check determinations were also made to prove that the addition of formaldehyde in this proportion did not interfere with the distillation and determination of ammonia by this method.

RICHARDS-WOODMAN METHOD FOR "ALKALINITY."

For the determination of the products of alkaline fermentation—"ammonia, or some substance which yields ammonia on distillation"—Richards and Woodman have published[1] the following method:

"*Alkalinity.*—Measure into a 750 cc. round-bottomed flask 25 cc. of the milk. Add 350 cc. of ammonia-free water and 0.5 gram of sodium carbonate and distil over about 200 cc. into a flask containing about 20 cc. of dilute sulphuric acid (1:40). Neutralize the distillate with sodium carbonate and redistil it, receiving the distillate into 15 cc. of N/10 hydrochloric acid. Titrate the excess of acid with N/10 sodium hydroxide."

It was thought that a comparison of the "alkalinity" figures obtained by this method with the "ammonia" figures obtained by vacuum distillation would be of interest, since each is designed to serve as a measure of the decomposition of proteid matter in the sanitary examination of milk.

In carrying out the Richards-Woodman process we adhered as closely as possible to the prescribed conditions and were careful to have the volume and alkalinity the same when the first distillate was redistilled, as in the original distillation. The result thus obtained, calculated as percentage of ammonia, is designated "Alkalinity figure A."

[1] "Air, Water and Food," New York, 1900, p. 152.

The liquid remaining in the flask at the end of the first distillation was restored to the original volume by adding 200 cc. of ammonia-free water and was again distilled until 200 cc. had passed over, this distillate also being caught in standard acid. Usually the volume was again restored and a third portion of 200 cc. distilled, but in most cases there was little difference in the amounts of ammonia found in the second and third distillates. Since the alkalinity of the second distillate is the result of decomposition which was doubtless also going on during the first distillation, the difference between the two might be interpreted as a measure of pre-existent ammonia or very closely allied substances. The alkalinity of the first distillate minus that of the second is designated "Alkalinity figure AA."

Determinations were also made in which the first distillate was caught directly in standard acid and titrated. The result thus obtained is given as "Alkalinity figure B." This result, corrected by subtracting the alkalinity of the second distillate, as just described, is designated "Alkalinity figure BB."

Naturally the alkalinity figure obtained by the Richards-Woodman method was, in each case, higher than the "ammonia" content as found by vacuum distillation. The table shows, however, that corrected alkalinity figures obtained by subtracting the alkalinity of the second distillate from that of the first are also almost always higher than the "ammonia" figures.

The redistillation recommended by Richards and Woodman does not seem to have a very marked influence, since the results obtained by distilling directly into standard acid are sometimes higher, sometimes lower and sometimes the same as those obtained by redistillation as in the published method.[1] The differences appear to be due mainly to the rate at which the distillation is carried on. If a sample froths badly, so that longer boiling is required to obtain the 200 cc. of distillate, the yield of ammonia is higher.

COMPARISON OF RESULTS.

Comparing the alkalinity figure obtained by the Richards-Woodman process with the ammonia obtained by vacuum distillation without the addition of salt, it will be seen that in fresh milk the former figure is several times as high as the latter. As the

[1] This point was tested in seventeen cases, the average of all the results being 0.0262 per cent. for "Alkalinity figure A" and 0.0250 per cent. for "Alkalinity figure B."

COMPARISON OF "AMMONIA" AND "ALKALINITY" FIGURES.

Sample.	Boussingault-Shaffer method[1] ammonia. Per cent.	Alkalinity figure A as ammonia. Per cent.	Alkalinity figure AA as ammonia. Per cent.	Alkalinity figure B as ammonia. Per cent.	Alkalinity figure BB as ammonia. Per cent.
Fresh milk "A"	0.0000	0.0079	0.0050	0.0066	0.0026
Fresh milk "A," pasteurized and kept five weeks at room temperature	0.0086	0.0191	0.0165	0.0175	0.0149
Fresh milk "B"	0.0007	0.0083	0.0050	0.0069	0.0036
Fresh milk "B," kept untreated four weeks in refrigerator	0.0069	0.0158	0.0135	0.0149	0.0124
Fresh milk "B," kept untreated seven weeks in refrigerator	0.0206	0.0300	0.0265	0.0318	0.0280
Milk + 0.1 per cent. formaldehyde, kept six weeks at room temperature	0.0013	0.0119	0.0089	0.0129	0.0099
Milk + 0.1 per cent. formaldehyde, kept twenty weeks at room temperature	0.0210	0.0277	0.0247	0.0260	0.0234
Contaminated milk + 0.1 per cent. formaldehyde, kept at room temperature for three weeks	0.0012	.....	.....	0.0063	0.0036
Contaminated milk + 0.1 per cent. formaldehyde, kept at room temperature for six weeks	0.0074	0.0096	0.0076	0.0092	0.0069
Contaminated milk, kept without preservative at room temperature six weeks	0.0098	0.0248	0.0235	0.0248	0.0235
Contaminated milk II + 0.1 per cent. formaldehyde, kept at room temperature one week	0.0063	0.0109	0.0069	0.0115	0.0085
Contaminated milk II + 0.1 per cent. formaldehyde, kept at room temperature five weeks	0.0124	0.0191	0.0168	0.0182	0.0152
Mouldy, decomposed milk	0.1122	0.1254	0.1139	0.1238	0.1122

[1] In these determinations the milk was not saturated with salt before heating with sodium carbonate.

milk ages both figures increase and in general at about the same rate, so that while the absolute difference is not greatly changed, the relative difference becomes much less. Relatively, therefore, the ammonia figure increases much more rapidly as the milk becomes stale than does the alkalinity figure.

Since the actual amount of nitrogen involved in the discrepancy between the two figures is in no case as great as the amount which is said to be present in the form of urea, the following experiment was made: A solution of pure urea was prepared of such strength as to contain 0.018 per cent. of nitrogen, this being the amount of "urea-nitrogen" found in cows' milk by Camerer and Soldner.[1] This solution was tested as in the Richards-Woodman process, with the modification described above. Twenty-five cc. were mixed with 350 cc. of water and 0.5 gram sodium carbonate and distilled, catching the distillate in standard acid until 200 cc. were obtained. The solution was then restored to its original volume by adding 200 cc. of water and another portion of 200 cc. distilled off. This was repeated until five successive distillates had been obtained. On titrating these distillates it was found that in each case 0.5 mg. of ammonia, or 0.002 per cent. of ammonia, calculated on the original solution, had distilled over. This is about the amount usually found in the second and third distillations in the examination of fresh milk by the Richards-Woodman process. This experiment indicates, therefore, that the discrepancy, due to urea, is practically eliminated by the method of correction used in obtaining the figures AA and BB above, and that in most cases the greater part of the discrepancy between the "alkalinity" and "ammonia" figures must be due to some other form of organic matter.

In order to study the influence of proteids, two samples, one fresh, the other seven weeks old, were treated with tannin to remove proteids and the filtrates distilled by the "ammonia" and "alkalinity" methods and by the modifications of the latter method above described.

So far as can be judged from these experiments, it appears that in fresh milk the discrepancy between the "ammonia" and "alkalinity" figures is due to the liberation of ammonia in the alkalinity determination, (1) from urea or some substance which behaves like it, (2) from proteid matter; for when the latter was

[1] *Ztschr. Biol.*, 1898, **36**, 277-313.

[1] In these determinations the milk was not skimmed

removed by tannin and the influence of the former was eliminated by subtracting the ammonia obtained by redistillation, as already described, the difference between the two figures disappeared.

With the old and partially decomposed milk the alkalinity figure was higher than the results of the vacuum distillation even after both these corrections had been applied. In this case, therefore, there seems to have been present some compound other than urea and not precipitated by tannin, which yields ammonia when boiled with very dilute sodium carbonate at ordinary, but not at reduced, pressure. In this case the removal of proteids lowered the amount of ammonia found by vacuum distillation, showing that the latter split off some ammonia from the partially decomposed, though apparently none from the fresh, proteids. It has already been stated that our later experiments showed a greater yield of ammonia from old samples when distilled without, than when distilled with, the addition of sodium chloride to lower the dissociation of the sodium carbonate.

As yet sufficient experiments have not been made to determine whether the cleavage of ammonia from decomposing proteid matter can be entirely prevented by the addition of salt, under the conditions of the vacuum distillation method as here described.

The determination of ammonia by vacuum distillation is, in our hands, a more delicate process than the alkalinity determination, and even if it does not always show the amount of ammonia which actually exists free in the sample, it has the advantage over the alkalinity figure of showing much greater proportional differences between pure and contaminated samples, or between the same sample when fresh and when stale or beginning to decompose.

COMPARISON OF ACIDITY AND AMMONIA.

While the time available for the present investigation was almost entirely occupied with the study of methods for determining ammonia or alkalinity, several determinations of acidity were made in connection with this work and two experiments were carried out with the purpose of comparing the development of acidity with the formation of ammonia in milk kept under ordinary conditions. These results may be shown by tabulation as follows:

	Acidity. Degrees.	Ammonia by vacuum distillation without salt. Per cent.	Lactic acid : ammonia :: 100:
First Experiment (milk kept at about 10° C.).			
Bottled milk July 7, 1904, as purchased	1.4	0.0005	0.4
Same sample one day after purchased..	1.6	0.0009	0.6
Same sample three days after purchased	9.4	0.0093	1.1
Second Experiment (milk kept at about 10° C.).			
Fresh milk, July 12, 1904, as purchased	1.7	0.0003	0.2
Same sample one day after purchased..	1.7	0.0005	0.3
Same sample two days after purchased	5.2	0.0005	0.1
Same sample six days after purchased..	10.2	0.0063	0.7
Same sample eight days after purchased	10.3	0.0078	0.8
Miscellaneous Samples (kept at room temperature).			
Fresh bottled milk June 15, 1904, as purchased	1—2[1]	0.0005	0.3—0.6[1]
Same sample after two days at room temperature	9.8	0.0112	1.3
Milk, five months old,[2] kept in cool, dark room unopened	29.2	0.0257	1.0
Duplicate[2] with formaldehyde 1:15,000[3]	29.2	0.0224	0.9
Duplicate[2] with 3 per cent. chloroform	2.5	0.0033	1.4
Milk,[4] two months old, with formaldehyde 1 : 1000	2.5	0.0009	0.4
Skim milk, eighteen months old, formaldehyde 1 : 1000[3] added when sample was two days old	4.9	0.0112	2.5
Milk with formaldehyde 1:1000, twenty weeks old, frequently opened	27.3	0.0205	0.8
Contaminated milk (see above), twenty weeks old, frequently opened	35.2	0.0233	0.7
Milk[4] + formaldehyde 1 : 1000; three years old[3]	15.9	0.0284	2.0
Milk[4] + formaldehyde 1 : 1000; four years old[3]	12.5	0.0386	3.4

Without attempting any detailed discussion of these results, it may be pointed out that they show great variations in the relative amounts of acid and ammonia depending upon the nature of the milk and the conditions under which it has been kept. So far as they go they confirm the view that the acidity and the am-

[1] In this case the determination of acidity was accidentally omitted. The limits given are estimated from the acidity determinations made on other bottles of milk from the same source.

[2] These samples of milk were put into clean sterile bottles within two hours after milking and remained unopened until they were examined five months later.

[3] When examined at the ages stated the formaldehyde had disappeared.

[4] These samples were treated with formaldehyde within two hours after milking, were opened for analysis within the next few days and after that remained closed at room temperature in diffused daylight.

monia content serve as measures of distinct types of fermentation, and that one may increase rapidly while the other increases slowly or not at all. A further study of some of these points has been undertaken in this laboratory.

SUMMARY.

The Boussingault-Shaffer method in which the sample is mixed with methyl alcohol, made alkaline with sodium carbonate and distilled under diminished pressure, has been slightly modified and found to be sufficiently delicate for the determination of ammonia in milk where the amount is often less than 0.001 per cent.

With an alkalinity corresponding to 0.5 per cent. sodium carbonate in the mixture of milk and alcohol, a cleavage of ammonia from organic matter appeared to be brought about by this process in the case of stale, but not of fresh, milk.

If the boiling mixture is saturated with sodium chloride to reduce the dissociation of the sodium carbonate, this cleavage is largely, if not entirely, prevented. The results thus obtained are believed to represent very closely the true amount of ammonia in the samples, while the amount of "cleavage ammonia," yielded by a sample when submitted to this process without the addition of salt, appears to be of value as an indication of the condition of the proteid matter.

Methods in which the milk is made alkaline and boiled under atmospheric pressure to expel the ammonia gave high results even when the dilution of the alkali was very great. Attempts to correct the results by subtracting the amount of ammonia given off in a second period of distillation were not satisfactory.

Preliminary experiments indicate that while milk ordinarily tends to develop both acidity and ammonia on standing, there is no necessary connection between the two, since either may increase rapidly while the other increases slowly, if at all.

QUANTITATIVE LABORATORY,
November, 1904.

[Contribution from the Analytical Laboratory of the Connecticut Agricultural Experiment Station.]

ON THE COMPOSITION OF AMERICAN NOODLES AND METHODS FOR THE ANALYSIS OF NOODLES.

By A. L. Winton and E. Monroe Bailey.

Egg-noodles are prepared by German housewives and reputable manufacturers from flour with the addition of eggs or egg yolks and salt. They are more or less yellow in color, according to the proportion of eggs used, whereas water-noodles, macaroni, spaghetti, vermicelli and other dough products prepared without eggs or foreign color are white or cream-colored.

Of late years unprincipled manufacturers have placed on the market so-called "egg-noodles" colored golden yellow with turmeric or coal-tar dyes but containing no eggs whatever or only very small amounts. As these dyes make the products appear better or of greater value than they really are, their presence without a declaration, according to the food laws of most states, constitutes an adulteration.

In 1901 tests for dyes and proximate analyses were made at this station on thirty-seven samples of macaroni, eight of spaghetti, ten of vermicelli and twenty-eight of noodles.

None of the samples of macaroni or spaghetti was artificially colored but two of the samples of vermicelli and twelve of noodles contained coal-tar dyes and ten of the samples of noodles contained turmeric. The coal-tar dye, except in one sample which contained a nitro-color, was an azo-dye related to the orange dyes commonly used as butter colors.

Judging from the percentages of fat and the reactions of the coloring-matter, only four samples of noodles contained an appreciable amount of eggs.

Since these analyses were made, Juckenack has described a method for determining the lecithin-phosphoric acid in noodles which has come into quite general use in German food laboratories. From the results obtained by this method may be calculated approximately the number of eggs or egg yolks per pound of flour used in making the noodles.

With the view of studying this method and developing methods for the detection of dyes as well as gaining some knowledge as to the composition of American noodles, analyses and examina-

tions for dyes have been made of twenty-two samples of commercial noodles found on sale in Connecticut, the results of which are given in the accompanying table.

ANALYSES OF AMERICAN NOODLES.

		In the water-free material.					
No.	Water.	Ash.	Protein (N × 6¼).	Nitrogen-free extract and fiber.	Fat.	Lecithin-phosphoric acid.	Color.
10718 Evidence of eggs	12.84	1.00	18.07	78.60	2.33	0.053	Turmeric
10470 " " "[1]	12.36	1.02	17.82	78.87	2.29	0.058	"
10672 " " "	12.91	0.65	17.57	79.95	1.83	0.046	Tropeolin
10829 " " "[2]	12.72	0.69	15.18	82.26	1.87	0.040	"
10674 " " "	13.59	0.73	16.21	81.12	1.94	0.036	"
10568 No evidence of eggs	13.66	1.19	14.53	83.63	0.65	0.015	Turmeric
10767 " " " "	12.79	0.79	17.12	79.59	2.50	0.029	Tropeolin
10569 " " " "	13.16	0.59	14.82	84.23	0.36	0.028	"
10368 " " " "	12.66	0.76	17.39	80.68	1.17	0.032	"
10781 " " " "	11.78	1.14	16.01	82.35	0.50	0.019	Turmeric
10798 " " " "	12.57	1.20	14.08	84.17	0.55	0.026	"
10759 " " " "	13.03	1.15	14.73	83.80	0.32	0.027	Tropeolin
10760 " " " "	13.16	1.28	14.39	83.72	0.61	0.025	Turmeric
10797 " " " "	12.49	0.61	14.92	83.84	0.63	0.024	Tropeolin
10717 " " " "	11.98	1.29	15.69	82.51	0.51	0.024	Turmeric
1981 " " " "	11.42	1.23	14.33	83.83	0.61	0.023	"
1980 " " " "	12.10	1.14	15.65	82.93	0.28	0.019	"
10784 " " " "	11.96	1.09	15.84	82.55	0.52	0.022	"
10785 " " " "	12.76	1.18	16.34	81.93	0.55	0.019	"
10675 " " " "	13.62	0.61	15.48	83.22	0.69	0.022	Tropeolin
10473 " " " "	12.27	1.21	14.32	83.79	0.68	0.023	Turmeric
10374 " " " "	13.02	0.49	13.92	85.20	0.39	0.018	Tropeolin

[1] Same brand as No. 10718.
[2] Same brand as No. 10672.

Juckenack's Method for Determination of Lecithin-Phosphoric Acid.—Wichelhaus[1] describes a method for the detection of yolk of egg in foods based on the extraction of lecithin with ether and the determination of phosphoric acid in the extract after its saponification. Juckenack finds hot alcohol a more efficient solvent for lecithin, his process in other respects being similar to that of Wichelhaus.

The details of Juckenack's method[2] are as follows:

Extract 30 grams of the finely ground material for ten hours with absolute alcohol in a Soxhlet extractor at a temperature,

[1] *Pharm. Ztg.*, 1890: Abs. Analyst, 1890, **15**, 116.
[2] *Ztschr. f. Unters. d. Nahr.- u. Genuss.*, 1900, **3**, 13.

inside the extractor, not below 55°-60° C. The extraction flask should be provided with a small quantity of pumice stone to prevent bumping during the boiling and the extractor enclosed by asbestos paper, if the desired temperature is not readily maintained. After the extraction is completed, add 5 cc. of alcoholic solution of potash (prepared by dissolving 40 grams of phosphorus-free caustic potash in 1000 cc. alcohol) and distil off all the alcohol. Transfer the residue to a platinum dish by means of hot water, evaporate to dryness on a water-bath, and char over asbestos. Treat the charred mass with dilute nitric acid, filter and wash with water. Return the residue with the paper to the platinum dish and burn to a white ash. Treat again with nitric acid, filter and wash, uniting finally the filtrates. Determine phosphoric acid by the usual method.

Juckenack calculated the percentages of ash, total phosphoric acid, lecithin-phosphoric acid and protein ($N \times 6\frac{1}{4}$) in noodles containing per pound of flour one to twelve eggs and one to twelve egg-yolks, assuming an average weight of the eggs and an average composition of both the eggs and the flour. Beythien and Wrampelmeyer,[1] also Sendtner,[2] later called attention to the importance of determining fat, as this constituent is present in but small amount in flour and the addition of only a single egg increases the percentage more than twofold. Juckenack and Pasternack[3] in a recent paper have substituted for the protein column in Juckenack's original table, which because of the variation of this constituent in the flour, is of little value, a column giving the percentages of fat (ether extract).

The following table is compiled from figures given in the tables named:[4]

Number of eggs per pound of flour.	Composition of the dry matter.				
	Ash. Per cent.	Total phosphoric acid. Per cent.	Lecithin-phosphoric acid. Per cent.	Ether extract. Per cent.	$N \times 6\frac{1}{4}$. Per cent.
0	0.460	0.2300	0.0225	0.66	12.00
1	0.565	0.2716	0.0513	1.56	12.99
2	0.664	0.3110	0.0786	2.42	13.92
3	0.758	0.3482	0.1044	3.24	14.81
*	* *	* *	* *	* *	* *
12	1.426	0.6123	0.2875	7.94	21.09

[1] *Zischr. f. Unters. d. Nahr.- u. Genuss.*, 1901, **4**, 145.

[2] *Ibid.*, 1902, **5**, 1018.

[3] *Ibid.*, 1904, **8**, 94.

[4] The German pound used in this calculation is approximately 468 grams. The avoirdupois pound is 454 grams.

Number of egg yolks per pound of flour.	Composition of the dry matter. Ash. Per cent.	Total phosphoric acid. Per cent.	Lecithin-phosphoric acid. Per cent.	Ether extract. Per cent.	N × 6¼. Per cent.
0	0.460	0.2300	0.0225	0.66	12.03
1	0.488	0.2720	0.0518	1.57	12.37
2	0.516	0.3127	0.0801	2.47	12.73
3	0.542	0.3520	0.1075	3.33	13.07
*	* *	* *	* *	* *	* *
12	0.745	0.6533	0.3171	8.64	15.71

According to these data our analyses show that only five samples (Nos. 10718, 10470, 10672, 10829, and 10674) contained appreciable amounts of eggs. Since Nos. 10718 and 10470 were sold under the same label as were also Nos. 10672 and 10829 the five samples represent but three brands. Accepting Juckenack's standards, none of the noodles with the possible exception of the first two samples, contained appreciably more than one egg or the yolk of one egg per pound of flour.

According to Jaeckle's experiments[1] the lecithin-phosphoric acid in noodles decreases considerably on long standing. For example, in water noodles the percentage decreased in eight months from 0.0220 to 0.0119, in noodles made with three eggs per pound of flour, from 0.1226 to 0.0607 and so on. On the other hand, the iodine number of the fat and also the percentages of fat increased with time, the latter, however, but slightly.

Juckenack's and Pasternack's and Sendtner's experiments do not bear out Jaeckle's conclusions, at least as applied to the commercial product, but a final verdict cannot be reaced until numerous experiments now in progress in European laboratories are completed.

Owing to lack of material we are unable to report results bearing on this point except on one sample (No. 10718). In the finely ground sample analyzed early in February, 1904, we found 0.0461 per cent. of lecithin-phosphoric acid while in the same ground sample, kept in the meantime in a glass-stoppered bottle, we obtained, late in October of the same year, 0.0431 per cent. These results indicate that no appreciable loss of lecithin-phosphoric acid was sustained on standing nearly nine months during the warmest seasons.

Since analyses made by Sendtner and more recently by Juckenack and Pasternack indicate that flour used for noodles may contain

[1] *Ztschr. f. Unters. d. Nahr.- u. Genuss.*, 1904, I, 513.

as high as 0.0533 per cent. of lecithin-phosphoric acid, there is little fear of injustice to the manufacturers, if the percentages of lecithin-phosphoric acid and fat are both taken into consideration in judging commercial noodles. It should, however, be remembered that fat may be added to noodles in some form other than in eggs.

Tests for Dyes.—Turmeric and nitro-colors are extracted from the finely ground materials by long-continued shaking with alcohol, and are identified by the usual tests.

The orange coal-tar dyes commonly employed are not dissolved by this treatment but are readily extracted by shaking with a mixture of 10 parts of alcohol and 1 part of hydrochloric acid. The dye designated "tropeolin" in the table is soluble in the acid alcohol, the filtered liquid being a rich orange color which, on evaporation at a gentle heat, changes to a rose-red. After a time this rose-red color also appears on the edges of the filter and in the extracted (but not washed) starchy residue. It disappears on addition of alcohol but reappears on drying. Ammonia changes the color of the extract to a golden yellow.

The color by Arata's test[1] dyes wool a dirty yellow which changes to rose-red on addition of acid. Concentrated hydrochloric acid added to the powdered material imparts a rose-red coloration. These reactions indicate that the dye is an azo-color closely related to methyl orange and is probably the same as Geissler and Crampton[2] find in butter colors.

The following analytical scheme applies to the colors thus far detected at this station in noodles and other similar products:

I. Yellow color extracted by 95 per cent. alcohol.

A. Filter-paper dipped in the concentrated alcoholic solution and dried becomes, on moistening with dilute boric-hydrochloric acid and drying, cherry-red, changing to blue-black with ammonia ..... *Turmeric.*

B. No cherry-red color obtained on the filter-paper when treated as under A, or else the color is not changed to blue-black with ammonia.

(1) Yellow color after evaporation of alcoholic solution soluble in water; solution partially decolorized by hydrochloric acid ..... *Nitro-colors.*

(2) Yellow color after evaporation of alcoholic solution insoluble in water..... *Egg color.*

[1] This Journal, **22**, 582 (1900).

[2] *Ibid.*, **20**, 110 (1898).

II. No yellow color extracted by 95 per cent. alcohol but an orange color extracted by a mixture of 10 parts of 95 per cent. alcohol and 1 part of concentrated hydrochloric acid. Filter-paper moistened with the acid-alcohol extract on drying at room temperature, becomes rose-red ..... *Azo-color* ("Tropeolin").

All of the twenty-one samples examined, including those containing eggs, were artificially colored. The color in twelve cases was turmeric, in ten was an azo-color of the nature described, which we have designated as "tropeolin."

As the color in the samples containing eggs conveys the impression that greater amounts were used than were actually present, these samples, like the others, must be classed as adulterated.

ON THE UTILIZATION OF FINE ORE, FLUE-DUST, DOWNCOMER-DUST, AND STOVE-DUST, IN THE BLAST-FURNACE.

By James C. Attix.

Received December 29, 1904.

At large furnace plants there accumulates vast quantities of these fine ores—flue-dust, downcomer-dust and stove dust—hereafter to be referred to as fine materials. It is quite a problem and considerable expense to get rid of them. Especially is this the case in the Pittsburg, Youngstown and Lake Districts, where the furnace burden is made up of from 40 to 75 per cent. of Mesabi ores. Not only is this the case where Mesabi ores are used to a large extent, but also at other furnace plants where other ores and especially concentrates are used.

It has been no small problem for furnace managers to work these fine materials. Many methods have been tried to get these fine materials in a shape to be utilized in the furnace and at the same time have the mass porous, or at least in such a shape that when they descend with the furnace burden they will not prevent the passage of the blast and gases.

Briquetting has been tried and given considerable notoriety, especially with the New Jersey concentrates, but so far as the writer has been able to learn, not a ton of these have been made

the past two years. This, by the way, is not because the briquettes do not work well in the furnace, but because a ton of them has thus far cost more than a ton of pig-iron has often sold for.

There is, however, I believe, one brilliant example of the briquetting process still in use and that is, or was, at the Joliet plant of the Illinois Steel Company. At this plant they were elegantly fitted to carry on this work. The furnaces were run to produce a certain composition slag among other things, and this slag was manufactured into cement, and a part of the cement-making materials were utilized to incorporate with these fine materials which were briquetted and dried and delivered to the furnace as a self-fluxing ore and formed a part of the regular furnace burden. They worked well and saved hundreds of tons of good, fine materials which otherwise would have been wasted.

These fine materials are not inferior in chemical composition to ores from which they are derived, in fact, many of them are of considerably better composition. Analyses of these fine materials at the Buffalo Union Furnace Company show iron 62.50, lime 7, carbon 5 per cent. Recent analyses of these fine materials at the Port Henry plant of the Northern Iron Company, very kindly supplied by Mr. L. D. Fraunfelder, chemist and assistant superintendent, show theirs to run iron 51, lime 8.25, and carbon 4 per cent. These materials show, upon analysis, that they are far too valuable to be thrown away. They are self-fluxing and carry a good percentage of carbon to partially reduce them.

Ore running from 50 to 62 per cent. iron, on the dock at Buffalo, is worth from $3.50 to $4.50 per ton.

With a 50 per cent. Mesabi mixture and the three furnaces running full blast there will be from 40 to 60 tons of these fine materials every twenty-four hours. Taking the average of 50 tons at $4.00, we have $200 worth of these fine materials per day.

It is useless to put them back in the furnace in their fine state for they will come over at once with the blast, if put in in small quantities, and if large amounts are filled at a time, they choke up the furnace, thus preventing the passage of the gases and causing the furnace to hang and slip.

The thing necessary then for the utilization of these fine materials is to incorporate them in something which will hold them until they get below the zone in the furnace where they can be carried over mechanically. Many materials have been tried and

quite a number patented for bringing this about. The principal substances employed in the lumping process are glue, tar, molasses, asphalt, etc.

Working along these lines, the writer decided upon the idea of using carbon—or coking these fine materials with bituminous coal. The coal in coking thoroughly incorporates the fine materials, acting as a fairly good carrier, being porous, takes the materials down to the zone of reduction and much of it still further to the tuyeres, carries more than enough carbon for reduction, carries no foreign materials into the furnace, and besides it is cheap. Samples have been made carrying 12½, 25 and 50 per cent. by weight of these materials. The 25 per cent. one, the mean shows, by analysis, to run:

	Port Henry. Per cent.	Buffalo. Per cent.
Iron	14.07	16.51
Lime	2.35	2.11
Magnesium	0.30	0.70
Alumina	2.00	2.30
Fixed carbon	61.28	65.25
Volatile matter	10.56	6.86

These tests were conducted in a clay crucible. The process can be carried on very nicely in a bee-hive oven. A small battery of these can be installed very reasonably and made to pay at a plant running four or more stacks. Any sized plant can be made to pay handsomely where the by-product ovens are used as they are at many plants to-day—and more are installing them. This plan is also applicable at any plant where the coke is made at or near the furnace.

I wish to acknowledge my indebtedness to Mr. L. D. Fraunfelder, chemist and assistant superintendent at Port Henry, N. Y., for his cooperation and analyses.

ON THE CRYSTALLINE ALKALOID OF CALYCANTHUS GLAUCUS.

By H. M. Gordin.

Received December 12, 1904.

Calycanthus glaucus (Willd.) is a shrub growing in Georgia, Notrh Carolina and Tennessee, where it is known as sweet-scented shrub, Carolina allspice or bubby. The seeds (achenes) of the plant are poisonous and have been known to kill cattle that

happened to eat them. They were examined for the first time by Dr. G. R. Eccles,[1] who found the seeds to contain about 39 per cent. of fixed oil and a crystalline alkaloid, which he named calycanthine,[2] and of which he described several characteristic color reactions. Later Dr. H. W. Wiley[3] also worked upon the same subject, examining both the oil and the alkaloid. He found in the seeds about 47 per cent. fixed oil, of which he determined the specific gravity, the iodine absorption and the refractive index. The absence of volatile acids from the oil was also established. Besides the oil and the alkaloid of the kernel of the seeds Dr. Wiley also examined the alkaloid present in the hulls and the very small amount of alkaloid dissolved in the oil when the latter is extracted from the seeds by petroleum ether. He also showed that the seeds are very rich in albuminoids and sugar, but very poor in starch.

As considerable time has elapsed since the work of these chemists I undertook the investigation of the subject, intending to examine the alkaloid, the oil and the other constituents of the seeds. In the present paper I wish to report upon the results which I have so far obtained in the examination of calycanthine, hoping to supplement the work by more results in the near future.

As a complete description of *Calycanthus glaucus* is given in the above-mentioned articles of Dr. Eccles and Dr. Wiley, I shall refer to these articles for the botanical description of the plant and pass directly to the chemical investigation of the subject.

The first step in the preparation of calycanthine was to establish, by assay, the amount of alkaloid present in the seeds, and then find, by experiment, the best method which would give results approximating those of the assay. The assay was carried out by means of Prollius' fluid in the usual way and showed the presence of about 2 per cent. of alkaloid in the deoleated seeds. It was found that cold alcohol extracted only about 29 per cent. of the alkaloid, whereas hot alcohol extracted about 75 per cent. It is possible that acidulated solvents or ammoniacal chloroform or ether would give a larger yield, but as it was deemed de-

[1] *Proc. Am. Pharm. Assoc.*, 1888, pp. 84 and 382.

[2] The alkaloid calycanthine, which is the subject of this paper, should not be confounded with the calycanthin obtained by Th. Hermann from *Calycanthus floridus*. Hermann's calycanthin is a glucoside, free from nitrogen, easily soluble in water with strong fluorescence and has the formula $C_{25}H_{28}O_{11}$ (*Jsb. d. Chem.*, 1868, p. 806).

[3] *Am. Chem. J.*, 1889, p. 557.

sirable to avoid the use of acids or alkalies with an alkaloid of unknown stability, it was decided to use hot alcohol for extraction. The method I have used then is as follows:

The seeds are ground up very coarsely and then extracted completely with petroleum ether or benzene. All the fixed oil is thus taken out, leaving the alkaloid. The deoleated seeds are dried at ordinary temperature until the color of the benzene or petroleum ether disappears. The drug is then again ground, but this time to a fine powder, which is exhausted with hot alcohol. From the alcoholic tincture the alcohol is distilled off completely and the thick residue extracted with water, slightly acidulated with sulphuric acid. A brown flocculent residue remains, consisting probably of the acids with which calycanthine is combined in the drug, mixed with calcium sulphate and colored by resinous matter. The alkaloid goes into solution as a sulphate.

The solution is filtered and the alkaloid precipitated from the clear filtrate by an excess of potassium hydroxide. A flocculent precipitate is formed at first, which, on standing over night, becomes crystalline and heavy, and settles to the bottom of the vessel. The impure calycanthine is collected on a filter, washed with water and dried at about 40° to 50°.

To see whether any alkaloid remains in the alkaline mother-liquor a portion of it was shaken out repeatedly with ether and the ether removed by distillation. Only a trace of alkaloid remained. Into another portion of the mother-liquor an excess of carbon dioxide was passed and the liquid again shaken out repeatedly with ether. On distilling off the ether again only a trace of alkaloid remained, showing the absence of alkali-soluble alkaloid in any appreciable quantity. Whether the seeds contain an alkaloid that is easily soluble in water, but insoluble in ether, I shall try to determine later.

The crude calycanthine, obtained as described above, was dissolved in ten times its amount of acetone, the solution filtered off from insoluble mineral matter (found to be mostly calcium carbonate formed from the calcium salts of the drug and the potassium carbonate present in the potassium hydroxide) and then mixed with a slight excess of strong sulphuric acid, previously diluted with five times its amount of alcohol. The sulphate of calycanthine, which is almost completely insoluble in acetone,[1] soon

[1] Calycanthine sulphate is so insoluble in acetone that on removal of the acetone and taking up with water no precipitate is obtained with Mayer's reagent.

settles in the form of fine, small needles. The sulphate is collected on a filter, washed with acetone and dried at 40° to 50°. The dry sulphate is dissolved in water and the alkaloid precipitated with potassium hydroxide. After the alkaloid settles it is collected, washed with water and dried at about 80°. The alkaloid is now almost perfectly white and has a crystalline appearance.

For further purification the alkaloid is dissolved in about twenty-five times its amount of boiling alcohol and to the solution is added an excess of sulphuric acid, previously diluted with five times the amount of alcohol. The calycanthine sulphate soon commences to crystallize in beautiful snow-white silky needles, which are very difficultly soluble in cold alcohol. After setting the liquid aside for two days the sulphate is collected, washed with alcohol and dried at about 80°. The sulphate is again dissolved in water and the alkaloid precipitated with potassium hydroxide. After washing and drying, the alkaloid is dissolved in ten times the amount of acetone and to the solution is added an amount of water equal to half the amount of acetone taken. In a few minutes the alkaloid commences to crystallize in brilliant, orthorhombic bipyramids, having pinacoid form. On standing over night, about 85 per cent. of calycanthine taken crystallizes out. The last operation is repeated several times until the melting-point remains constant.

Thus obtained calycanthine forms small, snow-white crystals of the above-mentioned form, containing 0.5 molecule of water of crystallization. By slow crystallization from hot alcohol the alkaloid can be obtained in large, hard crystals of the same form.[1]

On prolonged exposure to the atmosphere calycanthine assumes a yellowish tint without losing its water of crystallization. It melts between 216° to 218°, and if the tube in which the melting-point is determined is not too narrow, a slight effervescence can be noticed at this temperature. The water of crystallization is completely removed on drying the alkaloid three or four hours at 120°. Anhydrous, it melts sharply at 243° to 244°.

From the solution of its salts calycanthine is precipitated by alkalies, alkaline carbonates and ammonia, at first in a flocculent condition, but on standing a few hours the alkaloid becomes crystalline and heavy.

[1] The exact crystallographic measurements and the optical rotation of calycanthine and of some of the more important of its salts will be given later.

Calycanthine has a bitter taste and a slightly alkaline reaction towards litmus. It is so little soluble in water that Mayer's reagent, in the presence of acid, gives only a slight turbidity. It is slowly, but completely, soluble in ether or chloroform and difficultly soluble in benzene. The best solvents for calycanthine I have so far found to be acetone and pyridine.[1] The alkaloid forms beautiful, crystalline salts with all acids so far tried. It is a monoacid, weak base. It forms a neutral and an acid sulphate, of which the former becomes yellow on exposure to the air, whereas the latter does not change color. The sulphates and hydrochloride are extremely easily soluble in water, but almost insoluble in acetone. In alcohol the sulphates are very difficultly soluble. The hydrochloride requires about 15 parts of alcohol for solution. The nitrate, hydriodide and oxalate are difficultly soluble in cold water or alcohol. The acetate is extremely easily soluble in water, alcohol or acetone, but cannot be obtained in a stable condition, as on exposure to air it continually loses acetic acid, which can be noticed by the odor.

The aqueous solutions of the neutral sulphate and the hydrochloride are strongly acid to litmus paper, showing the alkaloid to be only weakly basic. Both the hydrochloride and the hydrobromide contain 1 molecule of water of crystallization, but the hydrobromide is comparatively stable in the air, efflorescing only slightly upon exposure to the air and losing its water of crystallization only slowly in the vacuum desiccator over sulphuric acid, whereas the hydrochloride commences to lose its water of crystallization immediately on exposure to the air, and in the desiccator the loss is much quicker than in the case of the hydrobromide. If a crystal of the hydrochloride or of the hydrobromide be put on a watch-glass in a desiccator containing sulphuric acid, the crystal very soon falls to a fine powder, either spontaneously or upon the slightest touch. Most of the salts, except the acetate, can be obtained almost quantitatively by treating an acetone solution of calycanthine with the corresponding acid previously diluted with alcohol or acetone. Both the crystalline and the anhydrous salts of hydrochloric and hydrobromic acids have nearly the same melting-points for both acids.

Calycanthine also forms a chlorplatinate and a chloraurate. The chlorplatinate crystallizes easily from hot water in long,

[1] The exact solubilities of the alkaloid and its salts will be given later.

orange-red aggregates. The chloraurate forms brown, microscopic needles, possessing strong pleochroism (yellow and orange).

The chloraurate is easily decomposed by cold water in the absence of hydrochloric acid or by hot water even in the presence of this acid, forming a deep violet colored solution from which gold is deposited on standing. It cannot be recrystallized from any solvent I have so far tried. It is very easily soluble in alcohol, but on slowly evaporating the alcohol the salt is partly decomposed. It is insoluble in ether. When calycanthine chloraurate is dissolved in alcohol in the presence or absence of hydrochloric acid, and ether added to the solution, beautiful long, silky needles soon commence to crystallize, but upon examination these needles were found to be not the gold salt, but simply calycanthine hydrochloride. This was shown by the fact that the needles were perfectly white, extremely easily soluble in water and left no residue upon calcination. The gold salt is possibly a mixture of several salts of different compositions and not a definite compound. It has no definite melting-point and continually, though slowly, loses weight on drying at 110°. Conditions under which a gold salt of definite composition is obtained I have so far been unable to ascertain.

All the salts of calycanthine so far examined lose some acid upon recrystallization from water or alcohol. It is therefore necessary to carry out their recrystallization in the presence of a slight excess of the corresponding acid.

With the volatile halogen acids it is not necessary to wash away every trace of free acid from the corresponding salts because these acids will be removed upon drying the substance in the air or in the desiccator over lime. But in the case of the nitrate the free nitric acid must be completely removed from the salt as otherwise the latter becomes dark green upon drying.

As shown by the following analytical data the formula of anhydrous calycanthine is $C_{11}H_{14}N_2$, hence calycanthine is one of the very few alkaloids that are crystalline at ordinary temperature and contain no oxygen.

Experimental.

Analysis of anhydrous calycanthine, $C_{11}H_{14}N_2$.

For analysis the alkaloid was dried at 120°. It then melted at 243°-244° and did not resolidify on cooling for quite a while.

1. 0.1655 gram substance gave 0.46255 gram CO_2 and 0.1226 gram H_2O.

2. 0.1668 gram substance gave 0.46418 gram CO_2 and 0.12185 gram H_2O.

3. 0.14142 gram substance gave 0.39129 gram CO_2 and 0.10015 gram H_2O.

4. 0.20178 gram substance gave 0.56302 gram CO_2 and 0.14412 gram H_2O.

5. 0.16537 gram substance gave 23.4 cc. N(t = 21°, b = 744).

6. 0.16745 gram substance gave 23.8 cc. N(t = 23°, b = 749).

Calculated for $C_{11}H_{14}N_2$: C, 75.77; H, 8.12; N, 16.12.

	Found.					
	1.	2.	3.	4.	5.	6.
C	76.21	75.89	75.46	76.10	.....	.....
H	8.30	8.19	7.94	8.01	.....	.....
N	.....	.....	.....	.....	15.76	15.78

ESTIMATION OF WATER OF CRYSTALLIZATION.

Dried in the air at ordinary temperature calycanthine melted at 216°-218°.

0.36915 gram substance lost on heating to 120° to constant weight 0.0184 gram.

1.3373 grams substance lost on heating to 120° to constant weight 0.0660 gram.

Calculated for $C_{11}H_{14}N_2.\frac{1}{2}H_2O$: 4.92 per cent. H_2O; found: 4.98 and 4.93 per cent. H_2O.

Calycanthine Hydrochloride, $C_{11}H_{14}N_2.HCl.H_2O$.—Two grams of the alkaloid were dissolved in acetone (20 cc.) and the solution mixed with an excess of strong hydrochloric acid (31 per cent.) previously diluted with twice its amount of alcohol. Almost immediately crystallization begins and on standing over night most of the hydrochloride crystallizes out. After washing with acetone and drying at ordinary temperature the salt was dissolved in about fifteen times its weight of boiling alcohol containing a few drops of hydrochloric acid and the solution set aside in a desiccator filled with quicklime. The hydrochloride soon commences to crystallize in large, heavy, rectangular plates containing 1 molecule of water of crystallization. An estimation of the water of crystallization after washing with alcohol acidulated with hydrochloric acid and drying at ordinary temperature showed that the salt loses its water of crystallization even on exposure to the air. 0.2832 gram

of air-dried substance kept in desiccator over sulphuric acid till the weight was constant (12 days) lost 0.200 gram.

Calculated for $C_{11}H_{14}N_2.HCl.H_2O$: 7.88 per cent. H_2O; found: 7.06 per cent. H_2O.

For the estimation of chlorine the salt was dried to constant weight over quicklime.

0.25605 gram substance gave 0.1756 gram AgCl.

0.3346 gram substance gave 0.2307 gram AgCl.

Calculated for $C_{11}H_{14}N_2.HCl$: 16.83 per cent. Cl; found: 16.96 and 17.04 per cent. Cl.

The hydrochloride after drying in the air melts at 212°-213° to a black liquid.

The anhydrous salt melts at 216°-217°.

A solution of the hydrochloride in alcohol or water assumes a yellowish color on standing.

Calycanthine Hydrobromide.—Made exactly like the hydrochloride, only substituting hydrobromic for hydrochloric acid, and has the same crystalline form.

Dried in the air the salt contains 1 molecule of water of crystallization and melts at 213°-214°.

0.28635 gram substance lost on drying over quicklime 0.0185 gram.

Calculated for $C_{11}H_{14}N_2.HBr.H_2O$: 6.59 per cent. H_2O; found: 6.46 per cent. H_2O.

For an estimation of bromine the salt was dried to constant weight over quicklime. It then melted at 216°-217° (same as the anhydrous hydrochloride).

0.26785 gram substance gave 0.1976 gram AgBr.

0.2309 gram substance gave 0.1700 gram AgBr.

Calculated for $C_{11}H_{14}N_2.HBr$: 31.33 per cent. Br; found: 31.39 and 31.33 per cent. Br.

A solution of the hydrobromide like that of the hydrochloride becomes yellow on standing.

Calycanthine Hydriodide.—Three grams of calycanthine were dissolved in about 30 cc. dilute sulphuric acid and an excess of a strong solution of potassium iodide added to the solution. A heavy curdy precipitate was formed which, when dissolved in hot alcohol containing some hydriodic acid, soon crystallized out in beautiful snow-white, silky needles. The hydriodide is difficultly soluble in cold water or cold alcohol but very easily soluble in hot

water or hot alcohol. It seems to contain no water of crystallization as its weight becomes constant after standing only twelve hours in desiccator, over sulphuric acid. It melts at 221°-222° and assumes a yellowish tint on exposure to light.

0.3093 gram of substance gave 0.2410 per cent. AgI.

0.26325 gram of substance gave 0.2047 per cent. AgI.

Calculated for $C_{11}H_{14}N_2.HI$: 41.99 per cent. I; found: 42.10 and 42.01 per cent. I.

Calycanthine Chlorplatinate, $(C_{11}H_{14}N_2.HCl)_2.PtCl_4.H_2O$.—Two grams of calycanthine hydrochloride were dissolved in 500 cc. hot water acidulated with hydrochloric acid and a slight excess of chlorplatinic acid dissolved in a little hot water added to the hot solution. On slowly cooling the liquid, beautiful, long, thick aggregates of orange-red color separated. Dried in the air at ordinary temperature, the crystals contain 1 molecule of water of crystallization and are strongly double-refracting. The chlorplatinate commences to change color at 222° and at 237° melts with decomposition. On drying at 110° for about four hours the water of crystallization is removed. The anhydrous salt is very hygroscopic.

0.35625 gram of substance lost at 110° 0.00835 gram.

0.93113 gram of substance lost at 110° 0.02095 gram.

0.1819 gram of substance gave 0.0452 gram Pt.

0.29835 gram of substance gave 0.07435 gram Pt.

0.2463 gram of substance gave 0.27115 gram AgCl.

0.23555 gram of substance gave 0.2596 gram AgCl.

Calculated for $(C_{11}H_{14}N_2HCl)_2Pt.Cl_4.H_2O$: 2.32 per cent. H_2O; 25.12 per cent. Pt; 27.41 per cent. Cl. Found: 2.34 and 2.25 per cent. H_2O; 24.85 and 24.92 per cent. Pt; 27.22 and 27.20 per cent. Cl.

Of the several other salts which I have made, the sulphate, oxalate, nitrate and picrate crystallize in very pretty forms. The results of their examination I hope to report in my next paper.

A chloraurate was also made but concordant results could not be obtained in its analysis, owing undoubtedly to the indefinite composition of this double salt. I shall try to find conditions under which a definite gold salt can be obtained.

An acetate was made as follows: 3 grams calycanthine were dissolved in 30 cc. of acetone and then mixed with 2 grams of glacial acetic acid previously diluted with 4 cc. acetone. The solution was

concentrated on a water-bath to about 10 cc., cooled and 30 cc. ether poured on the surface of the liquid. Very soon snow-white small plates commence to crystallize out. After standing over night the acetate was collected on a filter, washed with ether and dried in the air at ordinary temperature.

The acetate is extremely easily soluble in water, alcohol, and, unlike most of other salts of calycanthine, also in acetone, but almost insoluble in ether. On exposure to the light it becomes yellowish. It smells of acetic acid, which it continually gives off and has no definite melting-point, beginning to melt at 200° and becoming liquid only at 222°. This behavior of the salt indicating indefiniteness of composition, an analysis was not made.

Following is a list of color reactions which can be used for the identification of calycanthine:

1. If to a trace of calycanthine dissolved in very dilute hydrochloric acid a drop or two of a 5 per cent. gold chloride solution be added and the liquid made alkaline with sodium carbonate, a beautiful purple color is immediately produced, showing that the gold salt is quickly reduced. The value of this reaction consists in the promptness and extreme delicacy with which it occurs. While many alkaloids reduce gold salts in alkaline solution, I do not know of any other alkaloid that causes the reduction so quickly and in such extreme dilution. The reaction with calycanthine takes place with one part of calycanthine in a million parts of water.

2. Bromine water is first decolorized by a solution of calycanthine hydrochloride. If excess is added, a yellowish, flocculent precipitate is formed. If the addition of bromine water be stopped with the first appearance of a precipitate and the liquid filtered, a clear, colorless liquid is obtained which has a bluish fluorescence. If potassium hydroxide is added to this filtrate, a bulky, white precipitate is formed, which is insoluble in water and becomes gray when dried in the air.

3. Mayer's reagent gives a white, flocculent precipitate. Wagner's reagent gives a resinous precipitate. Tannic acid gives no precipitate either in neutral or acid solution. Marmé's reagent gives beautiful snow-white needles.

4. When Mandelin's reagent is put into a porcelain dish and a trace of calycanthine thrown upon the liquid, a magnificent blood-

red color is produced. After a few minutes the margin of the liquid assumes a green tint.

5. Potassium ferricyanide gives a white precipitate in concentrated solutions of calycanthine salts, but the precipitate dissolves when more water is added.

6. Potassium ferrocyanide behaves like the ferricyanide, but on heating the dilute solution of calycanthine hydrochloride to which some potassium ferrocyanide has been added, the clear liquid becomes turbid and assumes a greenish tint. After a few minutes a slimy precipitate separates out which is very difficultly soluble in water or alcohol.

7. On adding to a dilute solution of calycanthine hydrochloride a few drops of ferric chloride and then some potassium ferricyanide, Prussian blue is formed in a few minutes from the reduction of the ferri- to the ferro-salt.

8. Sulphuric acid colors calycanthine slightly yellow. If a few crystals of sugar be added to the mixture of the alkaloid with sulphuric acid, a beautiful pink color is produced.

9. Mercuric chloride gives a precipitate difficultly soluble in cold water, quite soluble in hot water, from which long, white needles separate out on cooling.

10. When calycanthine is heated to boiling for one hour with dilute hydrochloric acid the liquid soon becomes yellow, but has no odor. If the acid liquid is set aside, it becomes darker and darker. After ten days it becomes very dark red, but still has no odor. From this dark solution potassium hydroxide precipitates a yellow, flocculent precipitate insoluble in water or alkalies, extremely easily soluble in dilute acids and alcohol. The yellow substance emits a very agreeable odor when warmed with potassium hydroxide. Its solutions in acids has no odor.

11. Nitric acid brought in contact with calycanthine gives a beautiful green color.

12. Froehde's reagent colors calycanthine yellow at first, but the color becomes darker and darker on standing, until after about an hour it is almost red.

13. Picric acid gives beautiful, slender needles difficultly soluble in cold water, easily soluble in hot water.

14. Sulphuric acid and potassium dichromate gives a rose-red color.

Of the reactions here enumerated, those with nitric acid, sul-

phuric acid and sugar, sulphuric acid and dichromate were already observed by Eccles.

In order to test the physiological activity of calycanthine a few grams of the hydrochloride were sent to Dr. Cushny for experiments upon animals. The following is a preliminary report, which Dr. Cushny kindly sent me:

"Calycanthine hydrochloride was injected into the anterior lymph sac of a number of frogs of about 35 grams in weight. Smaller doses than 5 mg. had no definite effect; 5 mg. caused some clumsiness in movement without further change at first, but after twelve to twenty-four hours there was generally a very slight increase in the reflex irritability. The impairment of movement proved to be due to partial paralysis of the terminations of the motor nerve ends. Ten mg. induced more marked depression of the nerve ends, and after some hours this was accompanied by great increase in reflex irritability, the spinal cord appearing to be in the same condition as in strychnine poisoning, though the spasms were shorter, owing to the imperfect conduction of the impulses through the nerve ends. Fifteen mg. induced the same symptoms, but generally proved fatal to frogs of this size after one or two days.

"The drug was injected into mammals—cats and rabbits—hypodermically. Five mg. per kilogram had no distinct effect; 20 mg. per kilogram induced, after thirty to forty minutes, violent tetanic spasms, resembling those following strychnine.

"In several experiments the effect on the circulation was examined by means of the mercury manometer, when it was found that intravenous injection of 5 to 10 mg. per kilogram was followed by a marked fall in blood-pressure, with a very slow pulse and large oscillations. Atropine injection had no effect on these phenomena, so they must be ascribed to direct action on the heart. Similar changes in the heart-beat were found to follow the injection of calycanthine in the frog and turtle.

"In mammals, calycanthine seems to act as a stimulant to the spinal cord and as a depressant to the heart. In frogs it has, in addition, a weak, curare-like action on the terminations of the motor nerves. The symptoms are so similar to those described in cattle from poisoning with calycanthus that there can be no doubt that the alkaloid is the chief poisonous constituent."

NORTHWESTERN UNIVERSITY
SCHOOL OF PHARMACY.

AN IMPROVED GAS APPARATUS.

By J. E. Babb.

Received October 19, 1904.

The drawing and photograph represent some new features of the Orsat apparatus; in general design it is quite similar to the usual form.

For purposes of making a greater number of determinations and with a greater variety of gases six absorption tubes are em-

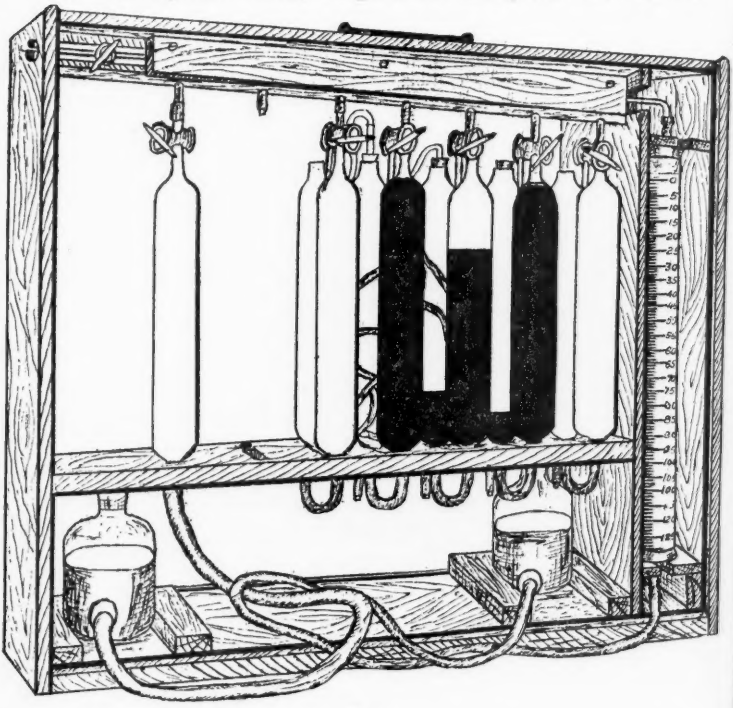

Fig. 1.

ployed, these being large enough to accommodate 250 cc. of absorbent solution in each tube, and an explosion tube is included.

The box is made to contain, besides the tubes, two dry cell batteries, one induction coil, an oxygen tank, and two leveling bottles—one for water to confine gases, and one for mercury to confine

gases for explosion. This necessarily makes the apparatus large, but at this it is only the size of an ordinary dress suit case.

The principal feature of the apparatus is the bubble tube shown in Fig. 2. It consists of two large tubes, back and front. The front tube consists of a capillary tube, *A*, placed inside of the large tube and connected with a three-way cock and at the top of the large tube.

In use, the three-way cock is engaged only with the capillary tube *A*. The gases then bubble through the absorbent solution. To return the gases to the measuring burette the three-way cock is engaged with both the capillary tube *A* and the exit tube *B*. The gas passes out through *B*, the solution rising up in the large tube and capillary tube *A* at the same level, the analysis being otherwise conducted as in the Orsat. By bub-

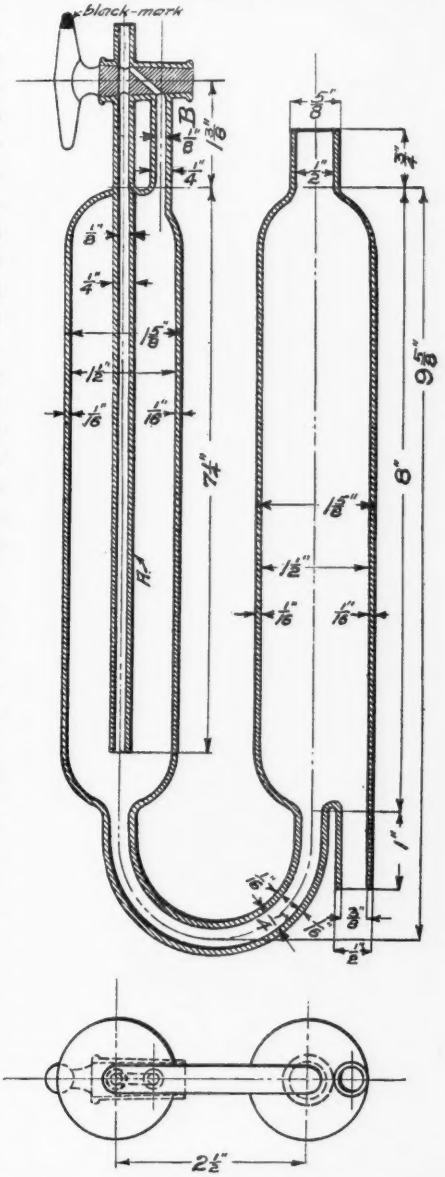

Fig. 2.

bling the gas through the absorbent solutions in this manner a more rapid and complete absorption of gases is obtained, and this is superior to absorptions by contact and shaking, one passage of the gases being sufficient for complete absorption.

A rapid analysis for gases for gas engine control can thus be made in twelve to fifteen minutes, including analysis for carbon dioxide, oxygen, carbon monoxide, hydrogen and methane, and ethylene.

The idea of bubbling the gas through the solutions has been suggested by many, and has been applied, but not in so convenient a manner.

WESTINGHOUSE MACHINE CO.,
EAST PITTSBURG, PA.

REVIEW.

SOME PRESENT PROBLEMS IN INDUSTRIAL CHEMISTRY.[1]

BY EDWARD HART.
Received December 29, 1904.

IT has often seemed to me that we spend too much time in telling about what we have done and what we expect to do. Progress consists, after all, in doing things and not in talking about doing them. It is, therefore, somewhat out of harmony with my own wishes to appear here to-day in a general discussion of the problems of industrial chemistry. Those of us who are engaged in industrial work must often choose between glittering generalities and silence. The conditions are happily expressed in a reply received from a well-known technical chemist in answer to my request that he write a paper for this meeting. "It is not necessary for me to say" he replied "that my relations to most manufacturers are of a confidential nature, and so I cannot divulge the information imparted to me. I regret that we are so hidebound here for there is much that would be of general interest. I am ashamed to say, however, that there are many manufacturers who distrust the consulting chemist who talks or writes much."

To the manufacturing chemist sulphur is of prime importance. Heretofore we have, on the Atlantic seaboard, depended largely upon Sicilian sulphur and upon pyrite, only a part of which was of domestic production.

To these sources have been added in recent years the gases obtained in the roasting of zinc blende from which sulphuric acid is now made in quantity. Quite recently it is announced that suc-

[1] Read at the Philadelphia meeting of the American Chemical Society.

cess has been attained in roasting pyrrhotite, of which vast deposits exist, among other places, in southwest Virginia. Most of the sulphur imported has been used in the manufacture of paper. The western deposits of sulphur have not been extensively drawn upon, owing largely to their distance from consuming centers. The Louisiana deposits have attracted much attention, however, and it is gratifying to learn that the courage and perseverance shown by Mr. Herman Frasch have at last met their reward. He informed me last September in New York that he was then taking out 16,000 tons of sulphur per month. He has taken out as much as 23,000 tons from one well. The existence of 40,000,000 tons has been proved. The holes are drilled to a depth of 800 feet and a 13-inch casing driven in. Inside this a 10-inch, then a 3-inch, and finally a 1-inch pipe are inserted. Between the 3- and 10- and the 10- and 13-inch pipes superheated water is forced into the well by its own expansive force. The sulphur melts and rises to 400 feet in the 3-inch pipe, from which it is raised to the surface by compressed air through the 1-inch pipe. The molten sulphur is run upon the ground in ponds made of rough boards 72 feet square and 14 feet high. The sulphur costs $2.90 f.o.b., per ton.

In the *Engineering and Mining Journal* of October 27th, I read as follows: "In brimstone the absorbing topic is the rapid development of the domestic industry. It is learned that large paper mills have contracted for Louisiana sulphur and the outlook for more business in this direction is promising. The paper mills are the largest consumers of Sicilian sulphur and should the syndicate lose these orders it can be said importation will eventually cease. While considering the expansion of the American sulphur mining industry it is of interest to quote the opinion of Emil Fog & Sons, of Messina, on the position of the industry in Sicily. In their circular of October 1st the Messrs. Fog state that they have warned the Anglo-Sicilian Sulphur Co. of the danger of serious competition with the Louisiana mines, only to be treated with scorn. Now the Sicilian market is startled by the news that a steamer with 3,000 tons of American brimstone has actually been shipped from New Orleans to Marseilles and that other shipments are to be made to Antwerp and Hamburg. The Chambers of Commerce of Girgenti and Caltanisetti are agitating for government intervention and at last the Anglo-Sicilian Co. has been aroused. Local newspapers propose to raise a fund of £2,000 by subscription as a premium to the inventor of new methods for the employment of brimstone. Curiously, nobody thinks of the only remedy, namely, a radical reduction in prices."

In the same journal for November 3rd occurs the following: "The Louisiana mines will ship this week from New Orleans the largest single cargo of sulphur—7,500 tons—ever consigned to New York. These mines are shipping about 800 tons daily and one day recently reported 860 tons."

It is evident that we have at one stride ceased to be dependent upon others for our sulphur supplies, indeed that we have become, commercially speaking, the only source of supply. Further than this, if the estimate of the cost of production above given is found to be borne out by further experience the owners of these mines will be in a position to drive both pyrite and pyrrhotite from the market. May the golden shower of sulphur thus rained upon the owners of the mines and upon the nation be wisely administered so that it may be a blessing to both!

In the nine months ending September, 1904, 107,343 tons of brimstone were imported for consumption, or at the rate of 143,124 tons annually. At $22 per ton this means an addition of $3,148,728 annually to our national wealth.

During the nine months ending September, 1904, we imported 32,934 tons bleaching-powder, 220,368 tons sodium nitrate, 126,392 tons common salt, 41,092 tons potassium chloride, 7,511 tons soda ash, 1,920 tons sal soda, 923 tons caustic soda, 5,071 tons saltpeter, and 42 tons potassium chlorate. These figures I have arranged in a column in the accompanying table setting over against each the imports for the corresponding periods in 1902 and 1903. I have added to the above items a number of others to be taken up in detail later on. These figures are from "Advance Sheets from Monthly Summary of Commerce and Finance," issued by the United States Department of Commerce and Labor for September, 1904.

	1902.	1903.	1904.
Bleaching-powder	43,677	40,994	32,934
Potassium chlorate	463	154	42
Sodium nitrate	147,980	208,740	220,368
Sodium chloride	148,094	123,941	126,392
Potassium nitrate	4,620	5,742	5,071
Potassium chloride	25,559	50,269	41,092
Soda ash	10,082	8,637	7,511
Sal soda	1,514	1,341	1,920
Caustic soda	1,273	1,072	923
India rubber, gutta percha, and gutta-julatonga	20,266	26,209	28,223
Argols or wine lees	11,412	9,978	8,349
Coal-tar colors and dyes, value in dollars	3,718,782	3,848,289	3,879,197
Glycerin	10,382	14,248	11,289
Logwood	44,422	31,195	27,458
Logwood extracts	1,278	1,293	1,140
Gums	28,262	31,620	27,513
Indigo	1,439	1,972	2,066
Pottery (dollars)	7,134,311	8,372,911	8,626,064
Glass (dollars)	4,518,603	5,147,260	4,450,195
Leather (dollars)	3,632,253	3,920,285	3,787,788
Plumbago	13,738	13,242	9,791

These figures, while by no means exhaustive, give a fair idea of the progress of our chemical industries. It is evident that we are rapidly increasing our domestic production of salt, bleaching-powder, potassium chlorate, soda ash and caustic soda and will soon be able to cover our own needs. In the nitrates no progress has been made and the same thing is shown in potash salts. In these two articles we can expect no improvement unless native sources of supply can be found. Such a source of supply for nitrate has been found in Death Valley, Cal., where, according to Bailey of the State Geological Survey, 22,000,000 tons have been located. I paid a visit to these deposits in the winter of 1901-2. At that time a considerable party was at work locating the deposits for the American Nitrate Co., of San Francisco. To a tenderfoot the prospect of obtaining nitrate from these deposits seemed rather remote. They were 80 miles from a railroad, in a barren desert with very little water and no fuel, with a very high summer temperature and at a great distance from consuming centers. To this the reply may be made that the same thing is true of the borax deposits of Southern California. The conditions are, however, not quite parallel. Borax sells at present for about 7½ cents per pound and carries a duty of 5 cts., while nitrate sells for less than 2½ cts., and is on the free list.

Another possible source of nitrate is to be found in the method which has been under experiment by the Atmospheric Products Co., of New York. According to the best information obtainable the cost of this product is still too high. It is to be hoped that some such process may ultimately prove successful. This is one of the present problems worthy of thought and experiment.

If our own nitrates could be made at home, we should add $11,000,000 to our national income.

Another problem is the finding of a source of potash to equal or excel the Stassfurt potash. It is true that certain companies in the United States have acquired interests in these deposits, which places them upon a better footing than formerly but it is very desirable that an independent source of supply should be found. Such a source of supply we have in the feldspar rocks which have a wide distribution. It does not seem hopeless to look to these as a source of potash. We often forget that with the extension of industrial chemistry new uses are being found for substances heretofore valueless such as aluminum and silicon. May it not be possible some day to extract the potash from such rock and to utilize the silicon and aluminum as well?

If we can now roast pyrrhotite, make sulphuric acid from the sulphur, extract the copper and sell the residue to the blast-furnace, the hope that we may some day make our potash at home is not necessarily an iridescent vision.

One of the most pressing problems is a substitute for India rubber. While new sources of supply have been found and the old

ones more carefully exploited, the use of rubber has increased more rapidly than the supply. With the advent of horseless vehicles this problem has become a really serious one, since the present great cost of the tire bids fair to seriously impede the growth of this industry. It has been found by experiment that the inflated tire for medium weight vehicles gives by far the best results in speed and power consumption. Let us hope that some future Acheson may do for the rubber industry what he has done for abrasives. In coal-tar colors and dyes the exhibit is not cheerful reading. Considerable progress, however, has been made during the two years just passed in various directions.

I do not at all despair of seeing the growth of an industry exceeding the German. Our imports of these articles do not, as it is, cut a very large figure in dollars, the total value for nine months being a little under four millions.

It is a matter of common knowledge that a large part of the glycerol thrown away in soap lyes ten years ago is now being recovered. Our home production must have increased enormously. Nevertheless, the figures given show that the importations are slowly increasing.

The decreased use of logwood is no doubt due to the increasing use of coal-tar dyes, especially the sulphur blacks, which have been found to be very satisfactory. Notwithstanding the growth of our own pottery trade the imports show a steady increase.

In glass the imports about hold their own. If methods now on trial for the manufacture of window glass prove successful, our export trade will no doubt increase; indeed our export trade in window glass though small even now shows a steady increase. In 1902 it amounted to $30,954, in 1903 to $43,320, and in 1904 to $56,710. In leather our imports remain practically stationary: $8,279,061 in 1902, $8,793,930 in 1903, and $7,968,723 in 1904. Our exports of unmanufactured leather for the same periods were $16,723,847, $17,673,082 and $18,916,558, and of manufactured leather $5,869,441, $6,685,288, and $6,688,792. In leather, then we are maintaining and increasing the lead we have held. If we remember that our own markets absorb constantly increasing quantities, the extent of our gain becomes evident.

Our production of plumbago, mostly artificial, seems still to be insufficient to meet our needs but the imports seem to be on the decrease. Probably this decrease will continue as the artificial product improves and the prejudice against it disappears.

Let us turn now for a moment to the products of the metallurgist: The imports of iron and steel excluding ore were for the three periods, $27,838,237, $34,652,234, and $16,591,000 while the exports were $73,352,000, $72,714,360, and $92,565,937. In 1903 we mined 32,471,550 tons of iron ore, produced a little over 18,000,000 tons pig iron and 4,500,000 tons of steel.

In this branch of industrial chemistry we are now acknowledged

leaders. The recent discovery of Mr. James Gayley bids fair to still further increase this lead. Mr. Gayley finds that simply drying the blast causes a vast improvement in the operation of the furnace—a much greater improvement than could have been expected. Should the most moderate expectations be realized and a saving of 50 cents per ton of pig be realized, the total saving will amount to $9,000,000 annually. Let us cherish such men. The man who can add such a sum to our income is not born every day.

Of copper we imported $8,205,737, $12,677,907, and $13,744,979, and exported $36,566,174, $29,906,841 and $53,485,906. This gain in output has been accompanied by considerable improvements in methods and diminished cost of product.

Of lead we imported $3,400,120, $2,867,637 and $2,132,485 and exported $590,311, $354,709 and $443,615. Here there is evidently room for improvement. The figures showing production tell a different story. In 1894 we turned out 159,331 short tons and in 1903, 280,000 short tons. The increase in production from 1902-1903, however, was not large, only 10,000 tons.

In zinc we imported $66,012, $46,680 and $37,088 and exported $363,150, $187,208 and $666,912. Our production was in 1901 140,822 short tons and in 1903 159,219 short tons. We produced 46,500 tons zinc oxide in 1901 and 62,962 tons in 1903.

The production of aluminum has increased from 7,150,000 pounds in 1901 to 7,500,000 pounds in 1903.

According to "The Mining Industry for 1903" we are now producing about three-eighths of the pig iron, three-sevenths of the steel, one-fourth of the lead, one-fourth of the zinc, one-fifth of the gold and one-third of the silver of the whole world. Do not these figures show that we have nothing to be ashamed of, rather we have cause for gratification at the present position occupied by those industries whose foundation stone is chemistry. The progress made cannot, however, be shown in figures—it is much greater than figures will show—there has been an enormous improvement in the quality of our products. This is shown in metals, in leather, in drugs, for which we have a deservedly high reputation, and in nearly all of our heavy chemicals. The pure chemicals in common use when I began this manufacture in 1880 could not to-day be sold. Indeed, many commercial chemicals can now be used by the analytical chemist without further purification. This improvement in quality has been accompanied by a decrease in cost of production. To-day most pure chemicals used by the analyst sell for less than a third of their cost in 1880.

Those of us who remember the manufacturing chemistry of twenty-five years ago, while conscious that there is still much to do, cannot help feeling very proud of what has been accomplished. What of the future? To rest is to rust, and of

that we are in little danger. Never in my recollection was the time so full of promise.

First, we are learning rapidly the need of coöperation. The manufacturer has need of the chemist, the engineer, the commercial man. Unless all concerned coöperate most cordially, success cannot be attained. Until the moneyed man learns patience and the chemist who dreams dreams and sees unsubstantial visions learns to touch the earth more frequently, this coöperation will not have been secured.

May we not hope and believe that many of us will live to see established in full operation here the greatest chemical industry the world has ever known? We have the natural resources, the market, the inventive genius, the commercial ability. To-day our great schools are turning out good chemists and we are rapidly learning to use them all to the best advantage. It would be foolish to ignore the great lead the old world, and especially Germany, has obtained in so many factory products, but this need not palsy our efforts. It is possible to regain what has been lost. It is impossible to believe that a free people, such as we, need fear any other in the industrial struggle. We have much to learn, but past experience shows that we can and will learn. Here are some more things to strive for:

1. It is desirable to find some cheaper way to burn cement. This, with steel, seems destined to be the great building material of the future and has already become of much commercial importance. Dr. J. W. Richards finds that nine-tenths of the heat used in the present method of burning is lost.

2. Better methods must be found for treating zinc ores. The metallurgy of zinc still belongs to the dark ages.

3. We must raise more of our sugar at home. We are enormous consumers and small producers of this important heat-producing food.

4. We must induce our farmers to fertilize their lands more heavily, so that we may at least restore to the land what is taken away.

5. We must make our own glass and our own pottery. We have already done much in this direction. Not the least important step forward is the formation of the American Ceramic Society. Much of our cheap ware is made at home, but the more expensive is mostly imported.

6. A beginning has already been made in what may be called organic industrial chemistry, but most remains to be done. It is humiliating to see to what an extent we are dependent upon the Germans and Swiss for such articles.

Several years ago I undertook to enter this field myself with two of my students who had just graduated. We found that there was a duty of 20 per cent. upon picric acid, and concluded this would be a good material with which to begin. We spent

many weary days working up a process fit for manufacturing, but finally found it and began to put our product on the market. We had marketed perhaps a ton of the material in small lots when some one in New York discovered that picric acid was not a dye but an acid imported for manufacturing purposes and therefore not dutiable, and to our astonishment and dismay succeeded in convincing our learned Treasury officials that such was the case. This, with a disastrous fire which came shortly after, convinced us that we were not yet ready to do up the Germans.

7. In Clarke's tables giving the average composition of the earth's crust, so far as known to us, the rare element titanium—as we used to consider it—figures as ninth in importance, making up as TiO_2 0.6 per cent.; strange as it may seem there is more titanium than phosphorus in the earth's crust. Of the ten elements there given, titanium alone has so far found little industrial use. A beginning has, however, been made by Peter Spence & Co., of Manchester, who had a most interesting exhibit at St. Louis.

It was not my purpose to attempt anything like an enumeration of all the industrial problems confronting the chemist. What has been said will be sufficient to convince those who are hunting trouble that much remains to be done.

NOTES.

Some Observations on the Use of Alkaline Waters for Laundry Purposes.—The attention of the writer has been called recently to a somewhat interesting condition which develops when strongly alkaline artesian waters are used for laundry purposes in steam laundries. The starched portion of a garment, when placed upon the steam rollers to be ironed, develops a deep yellow color. Fehling's solution gave a test for glucose, and iodine revealed the presence of dextrin. A probable explanation of this phenomenon then would be that the starch is converted into dextrin by the heat of the steam rollers; this in turn is converted into glucose, and the glucose reacts with the alkali present in the water, forming some alkali compound which has the deep yellow color. No complaint has come from the domestic laundries; probably because an ordinary flat-iron is not heated to a sufficiently high temperature to cause the reaction.

A partial analysis of the water was made with the following result:

Total solids	66.5	grains per gallon.
Chlorine	6.2	
Free ammonia	6.6	parts per million.
Albuminoid ammonia	0.01	
Oxygen consumed in moist combustion	0.675	
Hardness	3.8	

A quantitative analysis of the water residue was not made, but a qualitative test reveals the presence of alkali sulphates and carbonates in considerable amount.

It will be noticed that the amount of free ammonia is very great; considerable concern was at first experienced on this account, but every precaution possible was taken in the analysis, and the results were checked by the analysis of samples of known purity; the results obtained were very uniform and are probably correct. Wanklyn and Chapman, in their treatise on water analysis, are authority for the statement that such a condition is sometimes met with in deep waters that are organically pure.

As was to be expected, considerable trouble has been caused in the steam boilers by the use of a water containing so great an amount of solid matter.

As soon as attention was directed to the yellow color produced in the laundried clothes, efforts were made to find some method of neutralizing the alkali. The laundry process, as formerly used, was as follows:

Soak in clear cold water, pass into hot suds, then to a bleaching solution, rinse in hot water, pass into a sour bath acidified with oxalic acid, pass into a hot water rinse, pass into a hot bluing solution, rinse twice in cold water, once in hot water and again in cold water, pass into the starch solution and from the starch solution to the steam rollers to be ironed.

As modified for use with the alkali water the process is as follows: Soak in cold water, pass into hot suds, rinse in clear cold water, bleach in a hot solution, pass into suds again, rinse four times in cold water, pass into a cold bluing solution acidified with acetic acid, pass then directly to the starch and then to the steam rollers to be ironed. The principal difference is in what is known as the sour rinse, passing directly from that to the starch, thus giving no opportunity for the acid to be washed out, but, as it remains in the clothes, enabling it to neutralize the alkali and thus prevent the reaction with the glucose on the steam rollers.

This method gives excellent results with water that could not be used at all with the former method on account of the yellow color invariably produced.

I can find no mention of a similar phenomenon in any literature to which I have access. S. A. SKINNER.

The Determination of Sodium Carbonate in the Presence of Sodium Fluoride.—The ordinary volumetric method of estimating sodium carbonate by the use of standard acid and methyl orange cannot be employed in the determination of this compound in the presence of sodium fluoride.

If a trial titration were to be made of sodium carbonate in the presence of the fluoride, it is found that after the carbonate has been completely acted upon by the acid, the methyl orange indicator, instead of turning a distinct red, turns gradually into a darker shade of yellow, almost unnoticeable, and at an indefinite point, thus making this method worthless in a case of this kind.

A modification of the ordinary volumetric method which I have been using and have found to give excellent results, is outlined below.

One gram of the sample of fluoride is dissolved in about 100 cc. of water and to the solution is added 25 cc. of a 5 per cent. solution of calcium chloride, thereby precipitating calcium fluoride and also calcium carbonate, if there were any alkaline carbonate present.

The mixture is then titrated with N/10 hydrochloric acid, using methyl orange as indicator. As the number of cubic centimeters required by the calcium carbonate is equal to the amount required by the equivalent quantity of sodium carbonate, the per cent. of the latter may be obtained directly by multiplying the number of cubic centimeters of N/10 acid by 0.53.

The end reaction is very distinct and no difficulty is experienced in finding the point. It is very important that the solution of calcium chloride employed be perfectly neutral. If it should be found acid, add a few drops of methyl orange and dilute sodium hydroxide until neutral, and if found alkaline add methyl orange as before and dilute acid until neutral.

Barium chloride may be used in place of the calcium salt, but I give preference to the latter as the precipitate is not so dense and so gives a sharper titration. C. CHESTER AHLUM.

LANSDALE, PA.

NEW BOOKS.

THE RECENT DEVELOPMENT OF PHYSICAL SCIENCE. BY WILLIAM CECIL DAMPIER WHETHAM, M.A., F.R.S. Philadelphia: P. Blakiston's Son and Co. 1904. Price, $2.00.

Certain recent developments of physical science have taken two distinct directions, belonging to two different schools, with widely different tendencies. In one of these developments electric conduction through gases has been studied, the center of the work being the Cavendish laboratory of the University of Newton, and Clerk-Maxwell and Stokes. This study rests on atomic and molecular conceptions. From Faraday and Hittorf and Kohlrausch and Arrhenius we had learned that the conduction of electricity through solutions depends on the motion of electrically charged particles, called travelers or *ions* by Faraday. Similar is the explanation, recently put forth with confidence, of the conduction of electricity through gases; from this newer side of the subject striking results have been obtained. Electrolysis had suggested the notion of never-divided units of electricity, analogous to atoms of matter; the study of the conduction of electricity in gases is thought to have isolated these undivided units of electricity and to have submitted them to experimental study. These units of electricity have been called electrons by Stoney; and Larmor and Lorentz have developed a theory according to which atoms of matter are composed of electrons combined in varying numbers and different arrangements. Then M. and Mme. Curie added to our knowledge of the properties of atoms by their remarkable discoveries, and Rutherford had accumulated evidence pointing towards the disintegration of certain atoms and their transmutation into other substances.

In such studies we have to do with atomic and molecular conceptions in an extreme form; not only with atoms, but with the structure of atoms and with suggested orbital motions within the atom. But there are important parts of physical science whose methods dispense with the consideration of atomic conceptions. The great doctrine of the dissipation of energy has to do with molecules only in statistical aggregates, and need not inquire as to the parts which make up the aggregate. It is from considerations of available energy that Willard Gibbs has developed the complete theory of physical and chemical equilibrium.

Our author begins his account of recent researches in these two directions with a chapter on the philosophical basis underlying the whole magnificent structure, and asks whether our conceptions are life-like pictures of the reality behind the phenomena. He holds the balance fairly between the laboratory where there is no room nor time for philosophic doubt, and the hours of reflection in which we remember the purely conceptual nature of our scheme of Natural Science.

The second chapter treats of the liquefaction of gases and of the absolute zero of temperature As in the following chapters, principle and method are always prominent in the treatment; these are made easily intelligible with a certainty of touch and a facility which show expository powers of a high order. Our author sums up the interesting story of this chapter with the words, "The whole subject belonged to that branch of physical science which consists in recognizing and overcoming difficulties of manipulation, and, as it were, of asserting by force the superiority of mind over matter."

The following chapter treats of fusion and solidification. Explaining principles from the case of the familiar ice, he describes the methods and results of the study of alloys. The chapter contains a graceful characterization of the work of Willard Gibbs, in addition to another which is quoted from Larmor in the introduction.

In the fourth chapter, which treats of the problems of solutions, is seen how light on the dark places of a science may come from quite another science. The starting point of our present theory of solution was obtained by Pfeffer in a botanical laboratory. Then van't Hoff detected the law to which Pfeffer's measurements conformed, and put the theory on a sound basis. Whetham is perhaps the best known English supporter of modern views as to the nature of solutions, and it would be difficult to find a clearer or more interesting account of it, suited to the wants of the unprofessional reader, but also well worthy of consideration by the adept.

Three succeeding chapters treat of the conduction of electricity through gases, of radio-activity, and of atoms and ether. Not giving unimportant details, but attending chiefly to principles and methods, these 144 pages give what seems to the reviewer the

most interesting, the best balanced, the most successful exposition of these subjects which is accessible to that important fraction of the public which has an intellectual interest in the facts and inferences which are doubtless to add much to our knowledge of the structure of matter. A chapter on astro-physics makes a fitting conclusion to an excellent book. There are nearly forty illustrations, together with portraits of Newton, Lord Kelvin, Willard Gibbs, and van't Hoff.

HIGH-TEMPERATURE MEASUREMENTS. By H. LE CHATELIER AND O. BOUDOUARD. Authorized translation and additions by G. K. BURGESS. Second edition, revised and enlarged. New York: John Wiley and Sons. xiv + 341 pp., 79 figures. Price, $3.00.

It is but little more than four years since Messrs. Le Chatelier and Boudouard published the first independent handbook devoted exclusively to experimental pyrometry, the "Mesure des Températures élévees," Paris, 1900. Mr. Burgess translated this into English a year later, and now, after but a short interval, he finds it necessary to offer a second English edition containing nearly one-third new material. If we may accept this as a kind of barometric indication of the activity in all branches of research at high temperatures, it represents an altogether unprecedented interest in pyrometry and its applications.

The greatest advances in the interval since the first edition are to be found in the greatly increased accuracy with which the fixed points of the high temperature scale are now known, and in the extraordinary progress in optical pyrometry. The boiling-point of sulphur (444.6°) is now established securely within one- or two-tenths of a degree. Dr. Burgess expresses less confidence in the melting-point of gold (1065°) and suggests 5° as the limit of uncertainty. All the higher temperatures are still dependent upon extrapolation, but with several available methods and generally concordant results.

In the concluding chapter the suggestion is made to investigators that greater exactness and greater convenience of determination of the temperatures of common reference will be obtained by substituting the melting-points of chemically pure salts for those of the metals. The salts which are available for such a purpose are of such relatively low density and poor conductivity for heat that the phenomena attending change of state at high

temperatures are less sharply marked and less easy to interpret than one would desire in important standards for general use. There is always danger that error or misunderstanding may enter into their determination to such an extent as to outweigh the gain in convenience and in chemical purity. Better determinations of the melting-points of pure salts are certainly greatly needed, but to substitute these for the standard metals would seem to be a somewhat hazardous step.

The book contains an excellent account of the application of the laws of radiation to pyrometric measurement, together with most useful directions for the practical handling of the various forms of apparatus required, their sensitiveness and their limitations.

ARTHUR L. DAY.

MANUAL OF SERUM DIAGNOSIS. BY ROSTOSKI, TRANSLATED BY CHARLES BALDUAN, M.D. 12mo. vi+86 pp. New York: John Wiley and Sons. Price, $1.00.

There are two forms of pathogenic micro-organisms—one causing disease by producing specific toxines, the other affecting the health of the organism by the direct action of the germ on the surrounding tissue. The micro-organisms of the second group exercise a deleterious effect on the organism also in another manner. Although they do not secrete a toxine, their body substance contains one. This substance is liberated from the micro-organism only after their death and disintegration.

In the course of a bacterial disease the animal body develops protective substances. If the micro-organism causing the disease belongs to the first group, the substance is of the nature of an antitoxine, that means, it aims to neutralize chemically the toxine. In the second group of diseases the substances are lysins and agglutinins, acting as bactericidal substances.

The bactericidal and agglutinating power of the serum of a diseased or immunized animal or individual can be demonstrated also in a test-tube or under the microscope.

This property of the serum has been made use of for diagnostic purposes; the presence of agglutinating, or bactericidal power for a given micro-organism in the serum of an individual generally indicates the present or past infection with the same micro-organism.

This test was found most serviceable in the diagnosis of typhoid

fever, and is known as the Widal-Grüber test. The book of Rostoski contains the details of the test, and a critical review of the value and of the limitations of its application. Special attention is given to the relation of typhoid serum to paratyphoid micro-organisms, and it is justly urged by the author that in all cases of suspected typhoid the serum of the patient should be tested not only with the cultures of typhoid, but also with those of paratyphoid.

The technique of the test has recently been improved in such a manner that living micro-organisms are not longer needed for it. Thus it can be performed by every physician to whom the facilities of a laboratory are not accessible.

Also the details of these improved methods are given in the book.

Attempts were also made to apply the test for early diagnosis in tuberculosis. However, the nature of the micro-organism is so different from any other one that at present very few authors recommend the application of the agglutination test for this purpose.

In the course of plague, cholera, dysentery, paradysentery, glanders and many other diseases, the serum does develop bactericidal or agglutinating properties. Such sera have found application for the identification of the individual micro-organism, but thus far are of little value for clinical purposes.

In a special chapter the mechanism precipitating formation is described, and the forensic test of human blood is given in great detail.

In addition to the translation of the German text, Dr. Balduan has added Wilson's study of Grüber-Widal's reaction, containing a set of drawings illustrating the microscopical appearance of the reaction.

P. A. LEVENE.

THE TEXTILE FIBRES: THEIR PHYSICAL, MICROSCOPICAL, AND CHEMICAL PROPERTIES. By J. MERRITT MATTHEWS, PH.D., Head of Chemical and Dyeing Department, Philadelphia Textile School. New York; John Wiley and Sons. 8vo. vii + 288 pages, 69 figures. Cloth. Price, $3.50.

The publication of this book may be looked upon as an event worthy of record in the annals of textile literature. In our textile libraries will be found many volumes contributed from Germany,

France and England, but American publications along this line, possessing scientific merit, are comparatively rare. This American publication will, therefore, be received by many with interest and satisfaction. The author has succeeded in presenting the important facts in regard to the textile fibers, which have been discovered and noted by previous investigators and writers, together with many observations of his own, in a well-written and well-illustrated volume. The first chapter is devoted to the classification of the fibers. The source and properties of the various fibers and their action with chemical reagents is then discussed with detail, and their chemical composition is given as far as is known at the present time. A chapter is devoted to the mercerization of cotton and another to artificial silk. The book concludes with a discussion of the qualitative and quantitative analysis of the textile fibers. This analytical portion constitutes nearly a quarter of the book and is one of its most valuable features, and will undoubtedly prove a great aid to the textile chemist in solving the problems which often confront him.

The statement, "The subject of textile fibers has been lamentably neglected by chemists," made by the author in his preface is unfortunately too true, for the study of the physical properties of the textile fibers has been carried much farther than their investigation from a purely chemical point of view. Many important and unsolved problems present themselves along this line, and it is hoped that this book will prove to be an incentive, as well as an aid, to their future investigation. L. A. OLNEY.

LECTURES ON IRON FOUNDING. By THOMAS TURNER, Professor of Metallurgy in the University of Birmingham. London: Griffin and Company; Philadelphia: J. B. Lippincott and Co. 1904. 136 pp. Price, $1.50.

The book embodies a course of five lectures delivered at the School of Metallurgy of the University of Birmingham. The author discusses very concisely and in an interesting manner the fundamental facts as to the metallurgy of cast iron. The lectures deal consecutively with the following subjects: "Blast-furnace construction and practice, and the chemistry of the process"; "Iron founding"; "The relationship between chemical composition and physical properties of cast iron." The chemistry of the subject is made a leading feature of the book. In all metallurgical literature it is difficult to find a work which deals more concisely

and clearly, and in a more intelligent and attractive manner with the subject of pig iron. Many excellent illustrations add to the value of the book. Although designed for iron founders, the work will prove of especial interest to chemists. F. C. P.

MANUAL OF PHYSIOLOGICAL AND CLINICAL CHEMISTRY. By ELIAS H. BARTLEY, B.S., M.D., PH.G., Professor of Chemistry, Toxicology and Pediatrics in the Long Island College Hospital. Second Edition, Revised and Enlarged, with 47 illustrations. Philadelphia: P. Blakiston's Son & Co. 1904. Price, $1.00 net.

THERE is contained in concise form in this book the fundamental principles of physiological and clinical chemistry as adapted to the use of students and practitioners of medicine. The author's long experience as a teacher of chemistry in a medical school and as a practitioner of medicine has enabled him to select for inclusion in the book those subjects especially which bear upon the diagnosis and treatment of disease. This feature of the book makes it notably valuable to the medical man. The chemical methods are, in the main, well chosen; some, however, might well be replaced by newer ones which are more accurate, though more complicated. J. M.

FOOD INSPECTION AND ANALYSIS. For the use of Public Analysts, Health Officers, Sanitary Chemists and Food Economists. By ALBERT E. LEACH, S.B., Analyst of the Massachusetts State Board of Health. New York: John Wiley & Sons. 1904. Lg. 8vo. xiv + 787 pages, 40 full-page half-tones, 120 figures. Price, cloth, $7.50.

IT seldom happens that a new book on a comparatively new subject, after a critical examination, can be laid aside with the conviction, that the whole field of research, indicated by the title, has been completely and satisfactorily covered. This is the case, however, with the work under consideration. The arrangement of topics is excellent, the instructions are explicit and nothing essential seems to have escaped the author's notice. In a word, the book combines American *clearness* with German *gründlichkeit*. The book is divided into nineteen chapters, which treat of state control, the laboratory and its equipment, the function, proximate composition and nutritive value of food, general analytical methods, the microscope in food analysis and the analysis of all kinds of food products with methods of examination for adulterations.

One important feature of the work is the publication of stand-

ards of purity of foods so far as they have been established. These standards are helpful not only to the analyst but also to those engaged in the enforcement of pure food laws. Another useful provision is an exhaustive list of references at the close of each chapter.

The figures in the text illustrating apparatus and analytical methods will be appreciated, especially by chemists who are about to engage in food analysis for the first time. The same may be said of the excellent drawings showing the microscopical structure of spices, etc., as well as of the forty plates of photomicrographs at the end of the volume.

Finally the embodiment in the text of tables, which are in constant demand in food analysis, makes the book complete in itself and enhances its value as a convenient guide and work of reference in the examination of food products.

The compilation of methods and results, widely scattered through all kinds of publications, into a single volume together with the author's own large experience in food investigations has been a desideratum, and for this reason the work will doubtless be welcomed by chemists in general, and especially by those who are not in possession of the many sources drawn upon.

H. A. WEBER.

NOTES ON ASSAYING AND METALLURGICAL LABORATORY EXPERIMENTS. By RICHARD W. LODGE, Assistant Professor of Mining and Metallurgy in Massachusetts Institute of Technology. New York: John Wiley & Sons. London: Chapman & Hall, Limited. 1904. 8vo. viii + 287 pages. Illustrated. Price, cloth, $3.00.

This book is designed as a text-book for students who have already become familiar with the principles of chemistry, and is not intended for those who, without a previous knowledge of chemistry, desire to learn "practical assaying." Indeed there are a number of satisfactory books covering the subject sufficiently well for this latter purpose, but for those who desire information as to the principles involved, the variations in fluxes and manipulation necessitated by different materials, in short, those who really want to study the subject, this book is indispensable. Particularly valuable are the numerous tables of experimental data, such as those covering the effect of variations in the composition of the material assayed, and the losses in gold and silver during cupellation under various temperatures and conditions.

The author, in these tables, has freely used information from men who have had much practical experience, thus supplementing his own experience, which has evidently been largely that of the teacher.

The first twenty-two pages are devoted to the description of apparatus and reagents, and are followed by a chapter on sampling in which, as is the case throughout the book, the important points are in italics, which adds much to its value. Seventy-seven pages are devoted to the assaying of ores for silver, and fifty-seven pages to the assaying of ores for gold. A chapter on the fire-assay for lead follows, and the assaying of lead, silver and gold bullion is well, though briefly, treated. A short chapter on the assay of ores for copper and tin is followed by an excellent one on platinum and the platinum group, including a table covering the solubility of silver, gold and the rare metals, and also tables showing the loss of platinum during cupellation, its solubility when alloyed with various proportions of silver, and much other useful data. Much loose work has resulted from imperfect knowledge of the behavior of the platinum group when alloyed with other metals, which a careful perusal of this chapter should prevent.

The last chapter in the book on Metallurgical Laboratory Experiments and Notes is full of suggestion and indicates clearly the advantages of the use of small laboratory apparatus as a means of obtaining valuable information bearing on the metallurgy of ores.

This book should be in the hands of all those who are in charge of assay or metallurgical laboratories, as well as students of metallurgy for whom it was specially written.

WM. HOSKINS.

CORRECTION.

In the report of the Committee on Uniformity of Technical Analysis in this Journal for December, 1904:

On p. 1648 opposite chemist 3 under Sample C read 28.70 for 28.90.
On p. 1649 " " 26 " " A " 58.23 " 38.23.
On p. 1649 " " 30 " " A " 58.80 " 50.80.
On p. 53 lines 15 and 16 should be transferred to follow lines 17 and 18.